Modelling of microbiologically influenced corrosion in harsh environments

By

Nonso Ezenwa

A thesis submitted to

the School of Graduate Studies

in partial fulfilment of the

requirements for the degree of

Master of Engineering

Faculty of Engineering and Applied Science

Memorial University of Newfoundland

October 2018

St. John's, Newfoundland

To Nathan

Abstract

Microbiologically influenced corrosion (MIC) is one of the main causes of internal corrosion in oil pipelines and corrosion in oil wells. While many theories have been proposed to explain MIC, much about this form of corrosion remains poorly understood. At the heart of what is unclear about MIC is the role of surface deposits and biofilms in the process. To understand MIC, it is necessary to understand the changes that occur in surface deposits/biofilms. This can be achieved by two modelling approaches: deterministic modelling and molecular modelling. This thesis work employs the deterministic modelling approach to investigate the changes that occur in the electrochemistry of the biofilm as MIC occurs, which is then used to develop a predictive, time-dependent model of MIC. It also uses molecular modelling to examine the atomistic interactions that occur on the surface of steel materials. Both models are validated using published data from the literature.

Acknowledgements

I would like to express my deep gratitude to my supervisor and friend, Dr. Faisal Khan. His guidance, patience, motivation and assistance were invaluable in completing this work. My thanks also go to my co-supervisor, Dr. Kelly Hawboldt, without whose insight and guidance this work would not have been completed. I am grateful to Dr. Rick Eckert and Dr. Torben Skovhus who were kind enough to lend their considerable expertise from afar. Special thanks to my C-RISE family for giving me the platform to do this great work. Lastly, I would like to thank my son, Nathan, for being the motivation every step of the way. You make me smile everyday. Thank you for being the best!

Table of Contents

List of Figures

List of Tables

List of Abbreviations and Symbols

A = cross-sectional area (mm)

B = SRP pitting constant (in years)

c = the differential for action *j*

d = distance between atoms in the molecule (in Angstroms)

d_0 = equilibrium distance between the two atoms (in Angstroms)

$E_{bending}$ = in-plane bending energy (KJ/mol)

E_j = bond energy for action *j*

$E_{out\text{-}of\text{-}planeI}$ = out-of-plane bending energy (KJ/mol)

E_{steric} = steric energy (KJ/mol)

$E_{stretching}$ = stretching energy (KJ/mol)

$E_{torsionaI}$ = torsional energy (KJ/mol)

E_{vdW}= van der Waal energy (KJ/mol)

I = current density (A/m^2)

i_a = current density of anode

i_c = current density of cathode

k = Force constant

K = Proportionality constant

P = SRP pitting constant (in mm)

PR = pitting rate (in mm/year)

r = pit radius (mm)

t = time (years)

V_{FeS} = volume of FeS in biofilm

V_p = volume of pit

W = coefficient (with a value of 0.5)

x = pit depth (mm)

ε = van der Waal's potential of the interacting atoms (KJ/mol)

Chapter 1

Introduction

1.1 Background and Scope of Work

Microbiologically influenced corrosion (MIC) is defined as corrosion that is "initiated or accelerated" by microorganisms such as algae, bacteria and fungi (Borenstein, 1994). It has also been described as corrosion that is caused by the presence or activities of microorganisms (Little and Lee, 2007). While the effects of MIC in the oil and gas industry are widely acknowledged, data which highlight their negative impacts in the oil and gas industry are typically aggregated with the broader corrosion data. The cost of corrosion in the oil and gas sector is well known. It is estimated that the direct annual cost of corrosion to US oil and gas transmission pipelines is about $120 billion. This includes the cost of protective coatings, corrosion-resistant alloys, corrosion inhibitors, corrosion control services (Webster, 2010). In Canada, 80% of the cost of operating and maintaining the 350,000km of oil and gas transmission pipelines running through the country is corrosion-related (Webster, 2010). It is also estimated that as of 2013, corrosion mitigation, control and other associated costs equal about 3.4% of the global GDP (NACE International, 2016).

According to pipeline failure data for various onshore and offshore locations shown in the Table 1 below, corrosion accounts for up to 40% of asset integrity loss incidents (Palmer and King, 2008).

Table 1.1: Comparison of asset integrity loss incidents (Palmer and King, 2008)

	Reason for the incident %			
	Construction	Material	Third Party	Corrosion
Onshore	4	9	40	20
Offshore	6	8	36	41

From Table 1 above, it can be observed that corrosion is the biggest known cause of pipeline failure in oil and gas transmission networks. However, as corrosion is a broad subject caused by various mechanisms, a further breakdown of these numbers is helpful. Table 2 below identifies the various corrosion-causing mechanisms which result in pipeline failures inside oil and gas pipelines in offshore locations.

Table 1.2: Causes of internal corrosion in offshore oil and gas pipelines (Palmer and King, 2008)

Corrosion Failure Mechanism	Percentage
Carbon dioxide corrosion	32
Combined velocity and carbon dioxide corrosion	5
Chemical attack	1
Combined corrosion and fabrication defects	3
MIC	13
Corrosion of threaded items	11
Corrosion in dead legs	16
Erosion	8
Mechanical-associated corrosion failures	2
Corrosion fatigue	1
External corrosion	7

Some of the corrosion mechanisms in Table 2 are caused by agents or species contained in the pipeline effluent. In this category of corrosion-causing mechanisms, MIC is the third most important. This shows how consequential MIC is in the oil and gas industry. Recent incidents in oil and gas pipelines have been attributed to MIC. One such incident resulted in a leakage in Prudhoe Bay Field in Alaska in 2006, in which 200,000

gallons of oil spilled over 1.9 acres, recorded as the largest oil spill in the North Slope till date (Jacobson, 2007). The leak was caused by a 6.4mm by 12.7mm hole in an oil transit line. Due to the morphology of the pit and the suddenness of its occurrence, MIC was suspected. Another incident in the oil and gas fields of Western India yielded a sulfate-reducing bacteria (SRB) count of about 100,000 per 100ml, with cup-shaped and localized pits on the pipeline, a good indicator of MIC (Bhat, Khumar, Prasad and Katarki, 2011). Therefore, there is no doubt that MIC is a problem in the oil and gas industry.

The challenge with mitigating MIC in oil and gas infrastructure is that it is still poorly understood, with contradictory research results (Videla and Herrera, 2009; Zarasvand and Rai, 2014; Kip and van Veen, 2015). Some of what is insufficiently understood about MIC include the following:

a. MIC occurs in environments where corrosion is not expected to occur, such as in low chloride environments (Little and Lee, 2007; Skovhus, Andersen and Hillier, 2018)
b. Some microorganisms shown to cause or accelerate corrosion have also been shown to inhibit corrosion (Pedersen, Kjelleberg and Hermansson, 1988; Pedersen and Hermansson, 1989; Pedersen and Hermansson, 1991).
c. MIC rates can be much higher than regular corrosion rates, often exceeding 10mm/year (Skovhus, Andersen and Hillier, 2018).

Hence, to develop adequate measures against the occurrence of MIC in infrastructure used in oil production, transportation or storage, there is a need to better understand this phenomenon by investigating some of these issues, and this can be achieved by mechanistic and molecular modelling. This dual-track approach will help to shed light on both the mechanism of MIC and its effects.

1.2 Research Objectives

The objectives of this thesis work are listed as follows:

- Developing a molecular model of the MIC interface
- Validating the model using dynamics simulation, with boundary temperature data from the literature for trans-pacific heavy crude oil pipelines
- Developing a mechanistic model for the MIC rate, considering the effect of the main product of MIC – FeS – on the biofilm
- Validating the mechanistic model using MIC data from the literature
- Proposing MIC rate constants

1.3 Organization of thesis

- **Chapter 1:** The first chapter provides the background, motivation and the objectives of the research.
- **Chapter 2:** This chapter covers a literature review of MIC, MIC theories and MIC rate models.

- **Chapter 3:** A mechanistic model of MIC rate is proposed in this chapter, along with MIC rate constants.
- **Chapter 4:** This chapter proposes a molecular model for the MIC interface with assumptions drawn from experiments research in the literature.
- **Chapter 5:** This chapter contains major findings, conclusion of the work and recommendations for future work.

Chapter 2

Literature Review

2.1 An overview of microbiologically influenced corrosion

An overview of MIC is presented below under four thematic sub-headers. The purpose is to supply the reader with contextual and background information from the literature on important facets of MIC necessary for a better understanding of the issues discussed. First, the progress of MIC research over the last century is discussed. This is followed by a brief review of biofilms which are known to play an important role in MIC. Then, the known causative organisms linked to MIC are examined. Lastly, the theories which have been proposed to explain MIC and some predictive models based on these theories are introduced. Some of these theories and models are discussed more fully in the next chapter.

2.1.1 History

One of the earliest published works about the possible role of microorganisms in corrosion was by Gaines in 1910 (Videla, 2001). However, what is widely regarded as the pioneering work in establishing the electrochemical basis of microbiologically influenced corrosion came later in 1934. Kuhr and van der Vlugt, through a series of experiments, concluded that sulfate reduction, caused by “sulfate-reducing spirilla”, leads to the corrosion of underground cast-iron (Kuhr and van der Vlugt, 1934). Subsequently and for

decades after, most of the research in MIC focused on providing an experimental validation of Kuhr and van der Vlugt's theory of how MIC occurs, called the cathodic depolarization theory (Videla and Herrera, 2005). Booth and Tiller (1968) found through their experiment that the hydrogenase-positive bacterium, *Desulfuvibrio vulgaris*, stimulated the corrosion of carbon steel while the hydrogenase-negative bacterium, *Desulfotomaculum orientis*, was inactive. In another experimental study, it was determined that ferrous sulfide also plays a role in cathodic depolarization, and thus in corrosion (Booth, Elford and Wakerley, 1968).

By the 1980s, the awareness of the threat posed by MIC had increased to such an extent that it instigated a large-scale collaboration among diverse stakeholders and disciplines, from microbiology and materials science to chemistry and engineering, to combat the problem. This yielded a better understanding of issues like biofouling, ennoblement, MIC diagnostics and the electrochemical interactions on the corrosion interface. It also led to the development of new techniques for monitoring MIC such as ATP photometry and fluorescence microscopy, as well as SRB-detection methods such as the use of adenylyl sulfate (APS) reductase antibodies (Videla and Herrera, 2005). Within the last twenty years, there have been even more major advances in MIC studies such as the use of surface analysis techniques and microscopy to illuminate the role of sulfides in corrosion. More recently, molecular techniques involving the use of bacterial DNA and RNA have been used to identify dominant bacteria in biofilm consortia, calculate the

proportion of MIC-contributing bacteria and identify bacteria that are resistant to biocides (Videla and Herrera, 2005).

Hence, progress in MIC research has led to a greater understanding of the role of microorganisms and reactants in MIC. Biofilms embody these complex interactions between microorganisms, reactants and engineering materials, and is examined next.

2.1.2 Biofilms

Biofilms play an important role in MIC. They house many of the microorganisms and reactants that are known to initiate, accelerate or inhibit MIC (Beech and Sunner, 2004; Stevenson et al, 2011; Eckert, 2015). They can be described as heterogenous mixtures which are composed of water, extracellular polymeric substances (which include polysaccharides, proteins, lipids and nucleic acids), and metabolic products of microbial activity, such as small organic and inorganic compounds and enzymes (Sutherland, 2001; Eckert, 2015; Little and Lee, 2007). Biofilms contain sessile microorganisms which attach to substrates to initiate biofilm formation. These sessile microorganisms in the biofilm, and not the planktonic organisms in the bulk solution, have been shown to be responsible for MIC (Gayosso et al, 2004). The formation of biofilms on the surface of substrates is believed to occur in three stages, as shown in Figure 1.1: the attachment of the microorganisms to the substrate, their growth and then their eventual detachment (Little and Lee, 2007; Liengen et al, 2014).

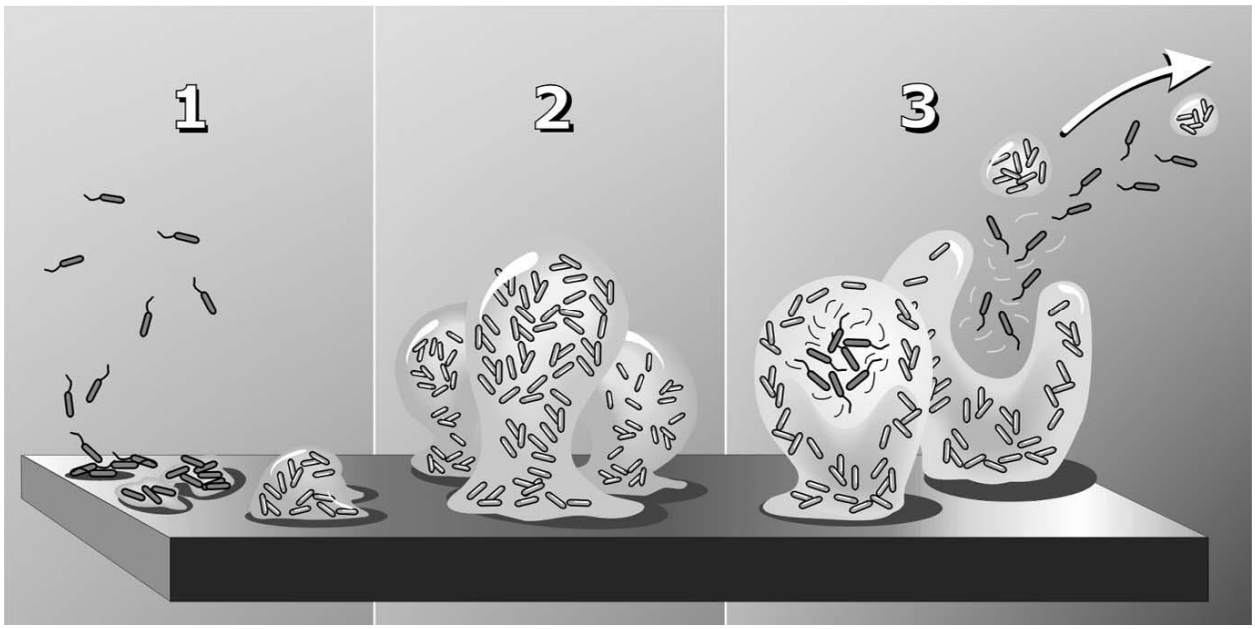

Figure 1.1: Biofilm formation on a substrate (Little and Lee, 2007)

Stage 1 in Figure 1.1 depends on the nature of the substrate's surface, the physiological state of the adhering microorganisms and hydrodynamics (Little and Lee, 2007). The growth of the microbial colony (stage 2) is influenced by factors such as the type of microorganism in the colony, the environmental conditions and gene expression, while detachment/dispersion (stage 3) is affected by nutrient levels and the flow velocity of the bulk solution (Liengen et al, 2014; Eckert, 2015).

2.1.3 Causative organisms

Microbiologically influenced corrosion is known to be mostly caused by bacteria. However, fungal activities have also been reported to initiate or accelerate MIC (Borenstein, 1994; Muthukumar et al, 2003; Little and Lee, 2007). Biofilms contain several

different microorganisms, and while individual microorganisms such as the sulfate-reducing bacteria (SRB) have been identified as causative agents of MIC, studies have shown that the most aggressive pits are formed where a consortium of these microorganisms exist (Little and Lee, 2007). Microorganisms linked to MIC are characterised in the Table 2.1 based on their oxygen requirement, engineering materials that they affect and their corrosion mechanisms.

Table 2.1: Common microorganisms identified as causative agents of MIC

Genus or species	Oxygen requirement	Metals affected	Metabolic process
Bacteria			
Desulfovibrio	Anaerobic	Iron and steel, stainless steel, aluminium, zinc and copper alloys	Use hydrogen in reducing SO_4^{2-} to S^{2-} and H_2S, promote formation of sulfide films
Desulfotomaculum	Anaerobic	Iron and steel, stainless steels	Reduce SO_4^{2-} to S^{2-} and H_2S
Desulfomonas	Anaerobic	Iron and steel	Reduce SO_4^{2-} to S^{2-} and H_2S
Acidithiobacillus ferrooxidans	Aerobic	Iron and steel	Oxidize Fe(II) to FE (III)
Acidithiobacillus thiooxidans	Aerobic	Iron and steel, copper alloys and concrete	Oxidize sulfur and sulfides to H_2SO_4; damages protective coatings
Gallionella	Aerobic	Iron and steel, stainless steels	Oxidize Fe(II) and Mn(II) to Mn(IV); promotes tubercle formation

Siderocapsa	Microaerophilic	Iron and carbon steel	Oxidize iron
Leptothrix	Aerobic	Iron and steel	Oxidize Fe(II) and Mn(II) to Mn(IV
Sphaerotilus	Aerobic	Iron and steel, stainless steels	Oxidize Fe(II) and Mn(II) to Mn(IV); promotes tubercle formation
Sphaerotilus natans	-	Aluminium alloys	-
Pseudomonas	Aerobic	Iron and steel, stainless steels	Some strains reduce Fe(III) to Fe(II)
Pseudomonas aeruginosa	Aerobic	Aluminium alloys	-
Fungi			
Hormoconis resinae	Aerobic	Aluminium alloys	Produce organic acids

2.1.4 MIC theories and models

Since 1934, some theories have been proposed to explain MIC. The earliest published MIC theory was the cathodic depolarization theory (CDT) proposed by Kuhr and Vlugt in 1934 (Kuhr and Vlugt, 1934). According to CDT, MIC occurs due to the de-adsorption of hydrogen from the surface of a metal (Xu, 2013). It comprises the following steps:

Step 1: $4Fe \rightarrow 4Fe^{2+} + 8e^{-}$ (Anodic reaction)

Step 2: $8H_2O \rightarrow 8H^{+} + 8OH^{-}$ (Dissociation of water)

Step 3: $8H^{+} + 8e^{-} \rightarrow 8H$ (Cathodic reaction)

Step 4: $8H \rightarrow 8H^+ + 8e^-$ (Cathodic depolarization by hydrogenase)

Step 5: $SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O$ (Sulfate reduction by SRB)

Step 6: $Fe^{2+} + S^{2-} \rightarrow FeS$ (Formation of corrosion product) (Al-Darbi et al., 2005; Borenstein, 1994)

Shortcomings of this theory in explaining MIC have been documented in the literature (Newman et al., 1992; Kakooei et al., 2012). The most important are that CDT ignores the importance of biofilm in MIC and fails to explain how hydrogenase-negative bacteria can cause corrosion (Newman et al., 1992).

The biocatalytic sulfate reduction theory (BCSR) was proposed as an SRB corrosion mechanism by Gu, Zhao and Nesic in 2009 (Gu, Zhao and Nesic, 2009; Xu, 2013; Xu, Li and Gu, 2016). According to this theory, the anode is the surface of the metal while the non-physical cathode is the cytoplasm of SRBs. It consists of oxidation, electron transport, reduction and by-product deposition. BCSR is further explained in chapter 3.

Based on these theories, some predictive MIC models have been developed to provide inputs for certain computations which are necessary to inform decision-making in the field. These models are discussed in detail in chapter 3.

2.2 Components of the corrosion interface

The MIC interface is the boundary between the substrate and the adhering biofilm. It is an important concept that is used in modelling. While biofilms have been discussed

earlier, a constituent of biofilms – iron sulfide – has been repeatedly identified as being critical in the interactions at the MIC interface. Hence, iron sulfide, and the other component of the MIC interface – the substrate – are examined next.

2.2.1 Iron sulfide

Iron sulfide (FeS) is an important component of the biofilm or the MIC interface. As MIC progresses, more FeS is deposited in the biofilm resulting in changes in the electrochemistry of the biofilm. This is modelled in chapter 3 where a time-dependent, deterministic MIC model is proposed. It should be noted that FeS is used loosely in the literature to refer to any of several FeS phases whose components are iron and sulfur. Different amounts of these phases have been identified in MIC but the predominant one is amorphous FeS (Ivarson and Hallberg, 1976; Watson et al, 2000). This is discussed in greater detail in chapter 3.

2.2.2 Substrate

The substrate in an MIC interface refers to the metal that is corroded by MIC. In molecular modelling, the Miller index of adatoms at the surface of a cleaved substrate surface need to be known. (This is not required in deterministic modelling). This index can then be inputted into any Molecular Modelling software with dynamics simulation capabilities (such as VASP, LAMMPS or Materials Studio) for molecular simulations. Different indices result in different surface properties of materials.

2.3 Molecular modelling

Molecular modelling can be broadly defined as any theoretical or computational technique that provides insight into the behaviour of molecular systems (Leach, 2001). It can also be described as the application of physical science laws to create molecular models and simulations with the purpose of determining the properties of molecules and the molecular systems they may be part of (Barril and Soliva, 2006). Molecular modelling is often wrongly presumed to be no more than molecular graphics, the display of computer-generated images of molecular geometry using visual representations such as "stick" or "space-filling". The fact, however, is that while visual imageries such as Dreiding's "stick" and the CPK "space filling" models are useful aids in relaying a concept which is often convoluted, molecular modelling involves more than the sketching of molecular structures; it is an iterative process that comprises molecular structure optimization, complex calculations and the inference of molecular properties (Leach, 2001; Coomba, Hambley and Martin, 2009). Molecular modelling is used to complement experimental research as illustrated in Figure 2.1.

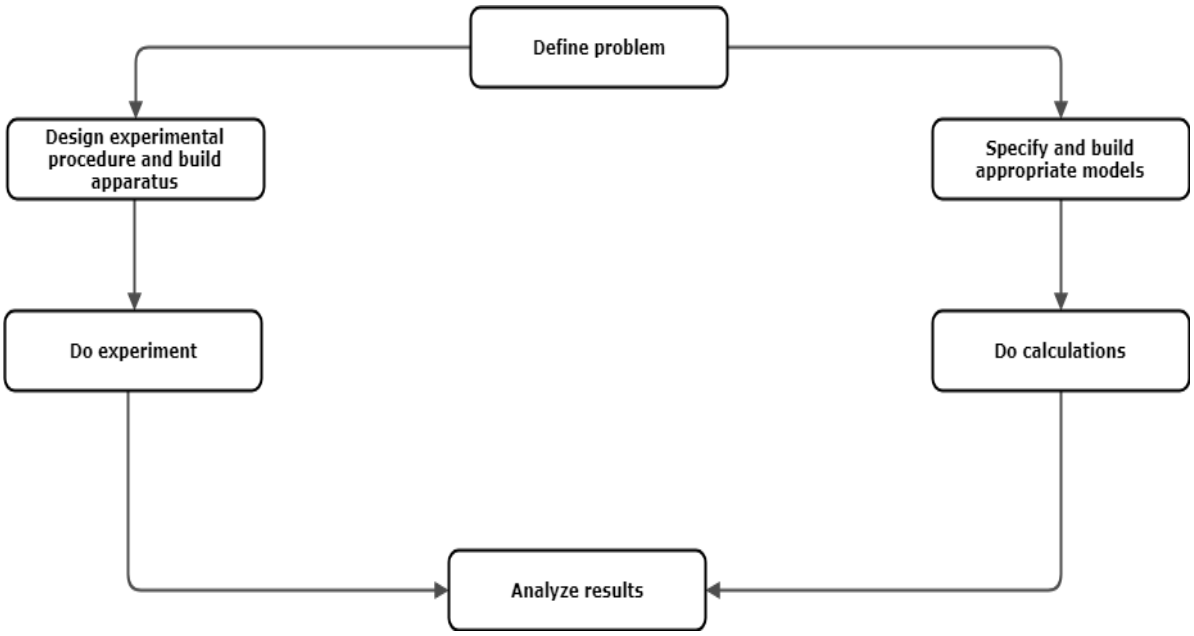

Figure 2.1: A comparison of experimental research and molecular modelling (Hehre and Schusterman, 2000)

Molecular modelling is not intended to be a replacement to scientific experiments. As shown in Figure 2.1, they play different, yet complimentary, roles in research. The origin of molecular modelling can be traced to some important advances early in the 20th century such as the development of diffraction techniques, the publication of Heisenberg's paper on the theory of quantum mechanics and Schrodinger's equation (Richon, 2008; Coomba, Hambley and Martin, 2009). Diffraction provided a detailed understanding of materials at the atomistic level by the elucidation of their crystal structures. This understanding gave a clear insight into the interrelationships between the structures of molecules which constitute materials and the properties of those materials (Gans et al, 1996). The purpose of molecular modelling is to derive one from the other.

Molecular modelling methods can be classified into molecular mechanical, semi-empirical and quantum mechanical methods. In many cases, molecular modellers use a combination of methods to achieve their goals. Because molecular modelling does not have a long history in corrosion science as it does in some other fields, these methods are examined in more detail.

2.3.1 Molecular mechanical methods

The goal of molecular mechanics (MM) is to find the lowest energy structure of a molecule, known as the equilibrium geometry. This can easily be done using most MM software. Molecular mechanics does not involve a solution of the Schrodinger equation. A knowledge of the underlying concepts is not required to perform molecular mechanical calculations, but it is presented here for a fuller appreciation of molecular modelling.

In the molecular mechanical model, atoms, which are assumed to be the smallest units of molecules, are held together by various inter-atomic forces (Coomba, Hamley and Martin, 2009; Taylor and Marcus, 2015). The bonded atoms in these molecules are modelled as balls being constrained by springs (bonds) using Hooke's law. Hence the energies that describe the behaviour of the bonds follow the form of a force applied on a spring. These bond energies include stretching, in-plane bending, torsional and out-of-plane bending, and they all follow the form $E = Wkc^2$, where:

E_j = Bond energy for action j

W = A coefficient (all these energies have a coefficient of 0.5)

k = Force constant

c = the differential for action *j*

The non-bonded energy in molecules in the molecular mechanical model is the van der Waal energy, E_{vdW}:

$$E_{vdW} = \varepsilon[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}]$$

Where E_{vdW} = van der Waal energy (in KJ/mol)

ε = van der Waals potential of the interacting atoms (in KJ/mol)

r_0 = equilibrium distance between the two atoms (in angstroms)

r = distance between atoms in the molecule (in angstroms)

The sum of the bonded and non-bonded energies of a molecule in a molecular mechanical model gives the steric or potential energy:

$$E_{steric} = E_{stretching} + E_{bending} + E_{torsional} + E_{out-of-plane} + E_{vdW}$$

Where, E_{steric} = steric energy

$E_{stretching}$ = stretching energy

$E_{bending}$ = in-plane bending energy

$E_{torsional}$ = torsional energy

$E_{out\text{-}of\text{-}plane}$ = out-of-plane bending energy

E_{vdW} = van der Waals energy (Coomba, Hambley and Martin, 2009; Williamson, 2017)

Steric energies are of little use in absolute terms and differ from software to software. However, relative steric energies between isomers of a molecule can be determined and compared with experimental results for reverse validation. Generally, MM can be used to determine the molecular geometries and energies of large molecules, which can then be used for feasibility studies and as inputs in molecular dynamics calculations (Lewars, 2016).

2.3.2 Semi-empirical methods

Molecular mechanics or the force field approach to molecular modelling does not provide any insight into processes that involve bond-making or bond-breaking – which is all chemical processes. This is achieved only by quantum mechanical (QM) or semi-empirical methods. Semi-empirical (or semi-experimental) methods have the advantage of being faster and using less computational power especially for large molecules like transition metal compounds, proteins or polymers (Jensen, 1999; Jensen, 2010). They replace some ab initio calculations with approximations or experimentally derived values

to reduce the computational power required. Some of the most common semi-empirical approaches used in the literature are AM1 (Austin Model 1) and PM3 (Parameterized Model 3) (Olson, 2000; El-Shafei et al, 2010; Fayet et al, 2010; Schwobel et al, 2010; Fassihi et al, 2012). They are based on first principle modifications such as neglect of differential overlap (NDO) and intermediate neglect of differential overlap (INDO) (Coomba, Hambley and Martin, 2009).

2.3.3 Quantum mechanical methods

There are two main approaches in quantum mechanical modelling – Hartree-Fock (HF) and Density Functional Theory (DFT).

2.3.3.1 Hartree-Fock

Hartree-Fock solves the Schrodinger equation to determine molecular properties by first calculating the preliminary orbital energy using the coefficients of atomic wave functions. An iteration of this process continues using the preliminary energy as an initial input until the results are consistent. Consequently, HF is also known as the self consistent field (SCF) procedure (Cowen, Karim and Piletsky, 2016; Lewar, 2016).

2.3.3.2 Density Functional Theory

DFT uses electron probability function instead of the wavefunction to calculate molecular properties. Electron density, unlike wavefunction, is a measurable parameter

and is a function of position only. (The wavefunction gets progressively complicated with an increasing number of electrons). The basis of DFT is that the electron density in atoms determines the ground state energy of the molecular systems they constitute, and hence other atomic properties can be ignored (Coomba, Hamley and Martin, 2009; Cowen, Karim and Plietsky, 2016; Lewar, 2016).

2.4 Applications of molecular modelling methods in corrosion studies

Many of the applications of molecular modelling in corrosion studies have been in corrosion inhibition (Ozcan and Dehri, 2004; Liu et al, 2010; Ju et al, 2016). The use of molecular modelling methods to shed light on the microscopic interactions occurring on the surface of the corroding substrate has not been studied extensively. In fact, after an exhaustive search, only two studies were identified in the literature (Nunomura and Sunada, 2013; Chew, Kuwahara and Ohno, 2018). With conflicting reports on the exact role of biofilm constituents on the corrosion rate, the simulation of the MIC interface using molecular modelling methods could help to further understand the underlying mechanisms involved in MIC.

Overview

This chapter has been sent to a research journal for potential publication. In order to meet the criteria for Master's thesis as required by the School of Graduate Studies at Memorial University, the formatting of this chapter has been revised to the format required for Masters thesis. The content, however, remains unchanged.

CHAPTER 3

Effect of FeS in the mechanistic modelling of microbiologically influenced corrosion rate

Nonso Ezenwa[a], Faisal Khan[a,*], Kelly Hawboldt[a], Richard Eckert[b], Torben Lund Skovhus[c]

[a)] Centre for Risk, Integrity and Safety Engineering (C-RISE)
Faculty of Engineering and Applied Science
Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada
[b)] DNV GL, 5777 Frantz Road, Dublin, OH, USA
[c)] VIA University College, Centre for Applied Research and Development in Building, Energy & Environment, Chr. M. Østergaards Vej 4, DK-8700 Horsens, Denmark

*Correspondance author: Email: fikhan@mun.ca; Tel: + 1 709 864 8939

3.1 Abstract

Many Microbiologically influenced corrosion (MIC) pitting rate models have been proposed. Though these models are useful, none incorporates the effect of iron sulphide (FeS), an important end-product of MIC, in modelling the pitting rate. Recent studies have provided a better understanding of the formation of FeS as a MIC end-product, its structure and properties. In the present work, this knowledge is applied to develop a mathematical model from the Gu-Zhao-Nesic model (Gu, Zhao and Nesic, 2009), considering the conductivity of FeS as an influencing parameter of the pitting rate. The model results are tested and verified using earlier published laboratory results.

Keywords: Corrosion; sulfate reducers; BCSR; biofilm; FeS; Microbiologically influenced corrosion

3.2 Introduction

Microbiologically Influenced Corrosion (MIC) is corrosion that is "initiated or accelerated" by microorganisms (Borenstein, 1994), and it is proposed to account for a significant portion of all corrosion (Xu, Chan and Fang, 2002; Yuan and Pekhonen, 2009; Skovhus, Eckert and Rodrigues, 2017). While microorganisms such as fungi and algae enhance MIC by the release of corrosive agents like organic acids, most of the microorganisms known to participate in MIC are bacteria and archaea (Borenstein, 1994; Muthukumar et al, 2003; Skovhus et al, 2012; Usher, Kaksonen and Macleod, 2014; Usher et al, 2014). The most studied MIC-causing bacteria are the sulphate-reducing bacteria

(SRB) which are reported to be responsible for approximately 75% of all MIC field cases that occur in oil pipelines (Al-Jaroudi, Ul-Hamid and Al-Gahtani, 2011; Manafi et al, 2013). Other MIC-causing bacteria include acid-producing bacteria (APB), iron-oxidizing bacteria (IOB), iron-reducing bacteria (IRB), sulphur-oxidizing bacteria (SOB) and manganese-oxidizing bacteria (MOB) (Muthukumar et al, 2003; Usher et al, 2014). Methanogenic archaea (MA) have also been found in significant numbers in corroding oil systems suggesting that they may play a role in MIC (Skovhus et al, 2012; Usher et al, 2014). It is estimated that the direct annual cost of corrosion to US oil and gas transmission pipelines totals about $120 billion. This includes the cost of protective coatings, corrosion-resistant alloys, corrosion inhibitors, cathodic and anodic protection, corrosion control services (Webster, 2010). In Canada, 80% of the cost of operating and maintaining the 350,000km of oil and gas transmission pipelines running through the country is corrosion-related (Webster, 2010). It is also estimated that as of 2013, corrosion mitigation, control and other associated costs equal about 3.4% of the global GDP (NACE, 2016).

Localized corrosion occurs in nonideal conditions of material structure and chemical composition. Pitting corrosion, a form of localized or non-uniform corrosion, is considered one of the most destructive types of corrosion as it usually affects a small area and therefore can go undetected (Jones, 1996; Roberge, 2000; Gan et al, 2016). Many studies in corrosion have focused on pitting corrosion (Caines, Khan and Shirokoff, 2013; Bhandari et al, 2015; Shekari, Khan and Ahmed, 2016).

While corrosion on a metal surface occurs due to a variety of independent mechanisms, both chemical and electrochemical in nature, pitting on an engineering material takes place due to electrochemical reactions on the surface of the material (Palmer and King, 2008; Xu et al, 2008). A metal surface and its environment, comprising the biofilm and the effluent, constitutes an electrolytic system. Electron loss occurs at the anode leading to the corrosion of the metal. When there is a strongly dissociable electrolyte as well as a good electron acceptor, this reaction is typically thermodynamically favorable. The electrolytic system can involve microorganisms. When pitting is initiated, facilitated or accelerated by microorganisms, it is commonly referred to as MIC pitting. MIC pitting rate models are important inputs in decisions made about oil and gas pipelines in the field.

Many of the MIC pitting rate models in the literature consider SRB as the only causative organism of MIC. Recent studies have highlighted the role of methanogenic archaea (Coetser and Cloete, 2005; Skovhus et al, 2012; Usher, Kaksonen and Macleod, 2014; Eroini et al, 2017; Tan, Goh and Blackwood, 2017). These MIC models based on SRB can be broadened to include other sulfate reducers present in the biofilm consortia on the substrate by removing the imposed limits that confine these models to the actions of SRB alone. As will be discussed later, these limits consider sulfate reduction and electron transport to be unique to SRB, which has been found not to be the case.

Several mechanisms have been proposed in the literature to explain MIC. The earliest published MIC theory was the cathodic depolarization theory (CDT) proposed by

Kuhr and Vlugt in 1934 (Kuhr and van der Vlugt, 1934). According to CDT, MIC occurs due to the de-adsorption of hydrogen from the surface of a metal (Xu, 2013).

Shortcomings of this theory in explaining MIC are well documented in the literature (Newman, Rumash and Webster, 1992; Kakooei, Ismail and Ariwahjoedi, 2012). The most important are that CDT ignores the importance of biofilm in MIC and fails to explain how hydrogenase-negative bacteria can cause corrosion (Newman, Rumash and Webster, 1992).

Table 3.1 shows some of the proposed mechanisms of MIC from the corrosion literature.

Table 3.1: Some proposed MIC mechanisms from the corrosion science literature

Corrosive process/substance	References
Cathodic depolarization by hydrogenase	Kuhr and van der Vlugt, 1934
Anodic depolarization	Obuekwe et al, 1981
Hydrogen-induced cracking and stress corrosion cracking	Edyvean et al, 1998
Sulfide	Fang, Xu and Chan, 2002
Biocatalytic sulfate reduction	Gu, Zhao and Nesic, 2009; Xu, Li and Gu, 2016

Aside from CDT, another proposed MIC mechanism shown in Table 3.1 is anodic depolarization (Obuekwe et al, 1981). According to this theory, the injection of nitrite or a strong oxidizing agent into crude oil leads to the formation of Fe^{3+} which results in the passivation of the metal surface. Subsequently, MIC occurs due to the removal of this protective Fe^{3+} covering to form an Fe^{2+} corrosion product. The authors sought to

demonstrate this theory in polarization and microscopic experiments using *Pseudomonas sp.* The main product of MIC in anodic depolarization is $Fe(OH)_2$ (Kakooei, Ismail and Ariwahjoedi, 2012). Hydrogen-induced cracking (HIC) and stress corrosion cracking (SCC) have also been suggested as possible mechanisms by which MIC failure occur (Biezma, 2001; Edyvean et al, 1998; Huang et al, 2011). Sulfide attacks have also been blamed for MIC though there is no consensus on how this takes place. Fang, Xu and Chan (2002) postulated that MIC occurs due to the depassivation of metal surfaces by sulfides produced by SRBs while Little and Ray (2002) argues that sulfide deposits accelerate MIC by altering the corrosion potential.

The most recent theory proposed to explain MIC is the biocatalytic sulfate reduction theory (BCSR). The MIC pitting corrosion rate model, due to SRP (sulfate-reducing prokaryotes), presented in this work is based on BCSR and hence this theory is examined in more detail.

3.3 The biocatalytic sulfate reduction theory

The biocatalytic sulfate reduction theory (BCSR) was suggested as a plausible SRP corrosion mechanism by Gu, Zhao and Nesic (2009). While that theory was initially proposed as an SRB corrosion mechanism, it is reasonable to believe that other microorganisms, particularly sulfate-reducing archaea (combined referred to as SRPs) which possess nanowires and hydrogenase complex enzymes may be involved in the two biotic stages in the BCSR pathway: Extracellular electron transport (step 2) and sulfate

utilization (step 3) (Thauer et al, 2010; Skovhus et al, 2012; Xu, 2013; Usher, Kaksonen and Macleod, 2014). Hydrogenase enzyme complexes are used for various energy-conversion processes under different conditions while nanowires are utilized for extracellular electron transport (EET) in microbial respiration, transferring electrons from extracellular solids to microbial cells (Thauer et al, 2010; Kato, 2015). According to BCSR, the anode is the surface of the metal while the non-physical cathode is the cytoplasm of SRPs. It consists of oxidation, electron transport, reduction and by-product deposition. These steps are explained below:

Step 1: The oxidation of iron at the surface of the pipeline resulting in a release of electrons

$Fe \rightarrow Fe^{2+} + 2e^-$, $E^0 = -447mV$ (Gu, Zhao and Nesic, 2009)

Step 2: The transport of the electrons released from step 1 to the biofilm, formed on the surface of the pipeline, by extracellular electron transfer.

Step 3: The reduction of sulfate in the cytoplasm of SRBs to HS^- (or to S^{2-} in a high pH environment). SRBs make up a portion of the microbial consortium in the biofilm. This reaction is referred to as the BCSR reaction and denoted by the equation below:

$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$, $E^o = -217mV$ (Gu, Zhao and Nesic, 2009)

$HS^- \leftrightarrow S^{2-} + H^+$

Step 4: The formation of iron (II) sulfide

$$Fe^{2+} + S^{2-} \rightarrow FeS$$

Electron mediation and SRB starvation experiments were performed to support this MIC mechanism (Xu, 2013).

3.4 MIC pitting corrosion rate models

It is not enough to only understand how MIC occurs but also important to know how quickly MIC takes place in any environment. This information is useful for scheduling pipeline inspections, pipeline replacements and even dig timing (Kiefner and Kolovich, 2007; Nessim et al, 2008; Caleyo et al, 2009; Vanaei, Eslami, and Egbewande, 2017). Hence, a reliable predictive mechanistic model of MIC pitting rate is an essential input in asset management.

There are only a few models of MIC pitting rate in the literature. MIC pitting rate models can generally be classified into two categories:

1) Models based on the mass transport of reactant and/or product species. Examples of these models from the literature include the Peng-Suen-Park model (Peng, Suen and Park, 1994) and the Al Darbi-Agha-Islam model (Al-Darbi, Agha and Islam, 2005). Both models are based on CDT. The Peng-Suen-Park model is a mathematical model of SRB pitting based on sulfate utilization by the anaerobes. The pits were divided into diffusion and reaction zones and sulfate was considered the rate-limiting reagent in the reaction zone.

Hence the rate of SRB pitting was dependent on the time for sulfate to diffuse through the first zone and reach steady state in the second. The Al Darbi-Agha-Islam model also uses diffusion and sulfate utilization mechanisms to model the SRP pitting rate in steel structures. The main difference between both models is in the initial conditions. A rectangular micro-pit was assumed to be the initial pit in the Al Darbi-Agha-Islam model while Peng-Suen-Park started with a microscale triangle. The Al Darbi-Agha-Islam model was applied to marine, freshwater and land environments in the same work.

2) Models based on the transport of electrons. An example is the Gu-Zhao-Nesic model, which is based on BCSR (Gu, Zhao and Nesic, 2009). In addition to kinetics and mass transfer, this model considers charge transfer as one of the important mechanisms involved in SRB pitting.

Because SRP corrosion is preceded by biofilm formation, the biofilm is believed to influence SRP pitting and the rate at which it occurs (Enning and Garrelfs, 2014). Hence, it is expected that variables such as species concentrations and charges will be prominent in most SRP pitting corrosion rate models (Peng, Suen and Park, 1994; Al-Darbi, Agha and Islam, 2005; Gu, Zhao and Nesic, 2009; Xu, Li and Gu, 2016). However, the role that FeS, the main product of MIC, plays in the dynamic biofilm environment has been absent from SRP pitting corrosion rate models.

3.5 The role of FeS in MIC

Iron sulfide (FeS) has long been of interest in corrosion studies (Newman, Rumash and Webster, 1992; Hamilton, 2003; Sun and Nesic, 2009; Enning and Garrelfs, 2014). The study of FeS is complicated by its loose definition. Several compounds whose main components are iron and sulfur are broadly referred to as iron sulfide in the literature. Many of these compounds (also known as phases) are inter-convertible at different temperature and redox conditions (Shu-Lin, Hui-Xian and Cheng, 2014). A clearer delineation of these phases is therefore needed, and this is illustrated in Table 3.2.

Table 3.2: Various iron sulfide systems from the corrosion literature (Sun and Nesic, 2009)

Compounds	Formula	Structure
Amorphous iron sulfide	FeS	Non-crystalline
Cubic iron sulfide	FeS	Sphalerite-type
Trollite iron sulfide	FeS	Distorted niccolite-type
Mackinawite	$Fe_{1+x}S$ (or FeS_{1-x})	2D layer material
Pyrrhotite	FeS_{1+x} (or $Fe_{1-x}S$)	Distorted niccolite-type
Smythite	$Fe_{3+x}S_4$ (or Fe_9S_{11})	Distorted niccolite-type
Greigite	Fe_3S_4	Thiospinel (magnetite-type)
Ferric sulfide	Fe_2S_3	Thiospinel with cation vacancies
Pyrite	FeS_2	Derived from rock salt
Marcasite	FeS_2	Isostructural with $CaCl_2$

SRP corrosion produces amorphous FeS as its main by-product, in addition to less significant amounts of the other compounds listed in Table 3.2. The amorphous FeS produced is transformed into mackinawite (also known as tetragonal sulfide or kansite) in excess H_2S (Ivarson and Hallberg, 1976; Watson et al, 2000). Mackinawite is an easily formed, non-toxic compound which is used to treat contaminated soils and underground water (Gong, Tang and Zhao, 2016). Other iron-sulfur phases such as greigite are also

produced (Morse et al, 1987; Gramp et al, 2010). Because the conditions required for this transformation exist in oil pipelines, it is reasonable to assume that various levels of iron-sulfur phases – amorphous FeS, mackinawite, greigite and potentially others – are found in corrosion products. However, the main ones are amorphous FeS and mackinawite and this study is limited to these two phases.

The role of FeS in MIC has been described as both protective and stimulating in the literature (Newman, Rumash and Webster, 1992; Hamilton, 2003). One of the earlier studies of the effect of FeS on MIC found that at high concentrations of H_2S (which occur at high corrosion potentials), FeS films form a protective layer over the metal which inhibits further corrosion by anodic passivation similar to the process caused by Fe_2O_3 (Newman, Rumash and Webster, 1992). At low H_2S levels, however, FeS deposition was reported to accelerate the pitting corrosion rate. This dual, antagonistic role of FeS in SRB corrosion has been supported by other studies (Booth, Elford and Wakerley, 1968; Jack et al, 1998).

Recent scientific progress in microbial fuel cells (MFCs) has helped to better understand the role of FeS in MIC. MFCs produce electricity from organic or inorganic waste materials (Malvankar, Tuominen and Lovley, 2012; Zhang et al, 2013). MFCs are biofilm-based and contain a microbial consortium constitutionally similar to that found in the biofilms of oil pipelines and therefore there is crossover into corrosion science. Two areas of research in MFCs have given insight into corrosion. The study of a wide range of organic materials and their derivatives has led to a more detailed study of the role of FeS

(Shu-Lin, Hui-Xian, and Cheng, 2014; Liu et al, 2017). Previously, it was challenging to determine key physical properties of FeS because of difficulties encountered in synthesizing pure samples of the compound. A re-focus on the material science of FeS in MFCs determined experimentally that FeS is in fact semi-conductive, contrary to previous beliefs. It was also established by resistivity studies that the conductivity of FeS increases with increasing temperature (Wang and Liang, 2007; Shu-Lin, Hui-Xian, and Cheng, 2014; Zhang and Moloney, 2016). This finding is one of the essential facets in this proposed approach to modelling the SRP pitting corrosion rate.

Second, MFCs increased the focus of research on the electrochemistry of biofilms. Malvankar, Tuominen and Lovley (2012) demonstrated a relationship between biofilm conductivity in MFCs and current density. One of the main challenges in MFC technology is the low power output which falls short in many practical applications. The experiment conducted by Malvankar, Tuominen and Lovley shows how current can potentially be generated in cells by altering the electrochemistry of the biofilms in the anode of the cells. Both advances in these two areas of MFC research have given rise to a new integrated approach to modelling the SRP pitting corrosion rate in oil pipelines.

3.6 An integrated approach

According to the Gu-Zhao-Nesic model proposed in 2009, the SRP pitting corrosion rate is:

$$PR = 1.16 i_a \text{ (A/m}^2\text{)}, \qquad (1)$$

Where *PR* = pitting rate in mm/y and i_a = current density of the anode

$$i_a = i_c, \quad (2)$$

Where i_c = current density of the cathode

In corrosion science, the average pitting rate can be determined by measuring the mean or maximum pit depths over time. Polarization techniques can also be used to estimate pit depth where the current density (or the corrosion current) is determined from polarization curves and used as the input in pitting corrosion rate models (Andrade and Gonzalez, 1978; Davydov, 2007). The Gu-Zhao-Nesic model is one of the pitting corrosion rate models that accepts the current density as an input.

The integrated approach is a modification of the Gu-Zhao-Nesic model which incorporates the effect of the changing electrochemistry of the biofilm, due to FeS deposition, on the SRP pitting corrosion rate. As SRP pitting corrosion occurs, the amount of FeS in the biofilm increases. The increase in the deposition of the semi-conductive FeS in the biofilm increases the conductivity of the biofilm which in turn leads to an increase in the current density. The increase in current density, according to the Gu-Zhao-Nesic model, positively correlates with the corrosion rate. Hence, as SRP corrosion occurs, the corrosion rate *should* increase. A mathematical model is developed from an expression of these interrelationships as below.

$$i \propto V_{FeS} \quad (3)$$

$$i = KV_{FeS} \quad (4)$$

Where V_{FeS} = volume of FeS in biofilm, i = current density, K = proportionality constant.

For model simplification, three assumptions are made:

1. Corrosion pits formed are cylindrical in shape
2. Pit formation occurs mostly downwards into the metal surface rather than across the metal surface (Davis, 2000). Thus, the cross-sectional area of the pit is assumed to be constant.
3. The predominant product of SRB corrosion is FeS. Hence, $V_p = V_{FeS}$

$$V_p = \pi r^2 x \quad (5)$$

$$V_p = Ax \quad (6)$$

Where x = pit depth, r = pit radius, A = cross-sectional area of pit and V_p = volume of pit

$$V_{FeS} = V_p \quad (7)$$

The Gu-Zhao-Nesic model for SRP pitting rate is:

$$PR = 1.16 i_a$$

The pitting rate here is the instantaneous rate not the average rate, and hence the above equation can be rewritten by combining (5) and (8) as:

$$\frac{dx}{dt} = 1.16 K V_p \quad (8)$$

Where x = pit depth, K = proportionality constant and V_p = volume of pit

Re-express (8) by combining with (6) to obtain:

$$\frac{dx}{dt} = 1.16KAx \quad (9)$$

Since A is assumed to be constant, replace K*A with a new constant B:

$$\frac{dx}{dt} = 1.16Bx \quad (10)$$

Solve this simple ordinary differential equation:

$$\int \frac{1}{x} dx = 1.16B \int dt \quad (11)$$

$$x = Pe^{1.16Bt} \quad (12)$$

Equation (12) is the general form of an exponential function where *x* = pit depth, *t* = time, and P and B are constants. The SRP pitting rate at any given time is the gradient of the tangent at the point that represents the time of interest.

3.7 A predictive model for SRP pitting

Hence, the integrated approach which incorporates the effect of FeS on MIC pitting rate produces a time-dependent model:

$$x = Pe^{1.16Bt}$$

Where *x* = pit depth (mm), *t* = time (years), *P* and *B* are SRP pitting constants with units of mm and years respectively.

The SRP pitting constants, P and B, can be obtained by fitting this model with experimental results to yield a matrix of P and B values for changing operational parameters known to affect the internal corrosion of oil and gas equipment, such as temperature, total pressure, partial pressures of gases like H_2S and CO_2, concentrations of species such as Cl^-, SO_4^{2-}, HCO_3^- (Papavinasam, Doiron and Revie, 2010). Pitting progression data from oil well tubing was collated by an unnamed offshore oil and gas production company using a Multifinger Imaging Tool (MIT) and provided to Mohd and Paik (2013). Oil well tubing is the innermost conduit of encased wellbores through which extracted oil and gas is transported from the reservoir. Due to the importance of tubing in oil production, numerous studies have been done to improve the corrosion resistance and mechanical properties of current tube materials (Liu et al, 2004). Earlier studies on the causes of corrosion on oil well tubing identified sweet corrosion and erosion of gas fluids as the main factors (Zheng, Zhao and Xu, 2001). However, recent studies have shown that MIC is an important factor in localized pitting of oil well tubing and offshore subsea structures (Larsen et al, 2011; Machuca, Bailey and Gubner, 2012; Machuca et al, 2013; Machuca et al, 2014). The composition of oil well tubing and the fluids transported are similar to those of other oil and gas equipment, particularly pipelines, and are therefore appropriate for generating the SRP pitting constants (Mohd and Paik, 2013; Revie, 2015). However, the data obtained from the Mohd and Paik study were only limited to pit depth and time. Therefore, the pitting constants are not correlated with the environment which is an important drawback.

Seven oil pipe segments and well tubing of various ages and three different grades – L-80, N-80 and AMS-28 – were used to obtain about 1437 pit measurements. The tubing was in use at subsea depths of about 2500 m. The corrosion data obtained given in Table 3.3.

Table 3.3: Corrosion data for oil well tubing (Mohd and Paik, 2013)

Age (years)	Mean pit depth (mm)
5.1	0.3300
5.8	0.3032
9.1	0.4086
11.7	0.4868
15.3	0.5856
18.2	0.7409
22.8	1.0210

Table 3.3 shows the mean pit depth over time for pit measurements taken in oil well tubing in an offshore subsea oil site.

The SRP pitting constants, P and B, can be obtained with this data. Figure 3.1 shows an exponential plot of pit depth versus the age of oil well tubing.

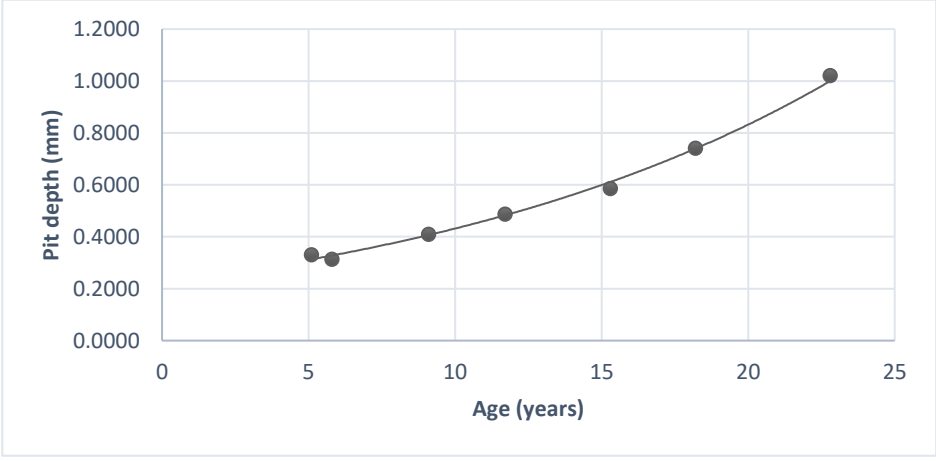

Figure 3.1: Graph of corrosion pit depth versus age of oil well tube

From Figure 3.1, the SRP pitting constants – P and B – are 0.224 mm and 0.0656 year respectively. These values were used below in model verification.

It is important to point out that the oil tubing data used to obtain the SRP pitting constants are not ideal. They were field data obtained from a secondary source which was provided by an unnamed company. Hence, other mechanisms of corrosion known to be present in oil fields, such as carbon dioxide corrosion, were not controlled. Also, no information was provided about the locations of the tubing within the oil field. It is unlikely that they were exposed to homogenous electrochemical environments, which means that the occurrence and the rates of pitting could have been affected from tubing to tubing. However, in the absence of lab data or other more reliable data, this was the best oil/gas equipment corrosion data that could be found.

3.8 Model testing and verification

To predict the progression of the mean corrosion pit depths in a location of an oil pipeline over time, equation 12 is used with the already determined SRP pitting constants. A case study from the literature is used to demonstrate the application of the proposed model.

3.8.1 Case study

In the Rivas, Caleyo, Valor and Hallen study (Rivas et al, 2008), 20 solutions of different compositions were prepared and used for immersion experiments to determine what kind of corrosive effect they had on stainless steel coupons. The solution that caused

the least uniform corrosion as well as the deepest and most number of pits with was selected as the experimental solution. Coupons from API-5L X52 pipeline steel were immersed in a plastic tank containing this experimental solution and the pit depths were measured over a 30-day period. The experimental solution was intended to simulate conditions in pipeline environments.

Table 3.4 shows relevant experimental data. Table 3.5 shows the measured pit depths over the 30-day exposure period and the predicted pit depths using the proposed model.

Table 3.4: Characteristics of experimental solution (Rivas et al, 2008)

	SO_4^{2-} (ppm)	Cl^- (ppm)	pH
Mean	156.98	21.34	6.17

Table 3.5: A comparison of experimental and predicted pit depths

Exposure time (days)	Study mean pit depth (mm)	Predicted mean pit depth (mm)
1	0.023	0.2240
3	0.029	0.2241
7	0.053	0.2243
15	0.072	0.2247
21	0.085	0.2250
30	0.104	0.2254

The model prediction in table 3.5 shows the limitations of the model when applied to short exposure times.

3.9 Discussion

The proposed model presents a novel framework for a time-dependent MIC pitting rate model derived from the basic principles of corrosion electrochemistry. It demonstrates that FeS deposition affects the MIC pitting rate and that owing to this, pit growth increases exponentially with time, not linearly. Figures 3.2 and 3.3 use MIC pitting data from oil well tubing to illustrate this.

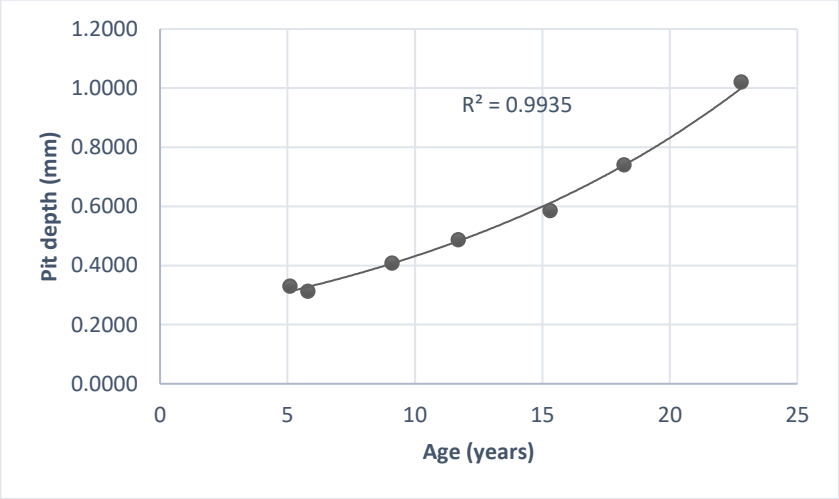

Figure 3.2: MIC pitting data with an exponential trend line

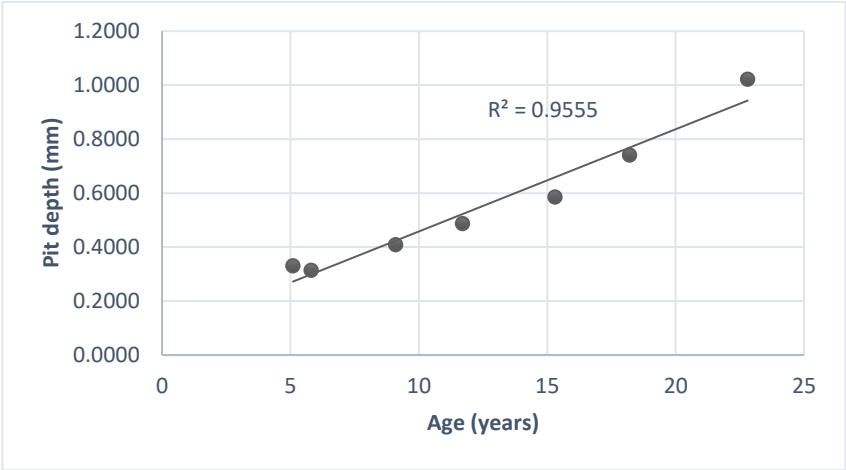

Figure 3.3: MIC pitting data with a linear trend line

Figures 3.2 and 3.3 show that MIC pitting data from oil well tubing achieve a better fit with an exponential trend line than a linear one. This provides some justification for this model.

Inputs into the model are time and exogenous factors known to affect MIC pitting such as temperature, pressure, pH, partial pressures and concentrations of the effluent species, which are represented by the SRP pitting constants. The main shortcoming of the proposed model is in the generated SRP pitting constants. The constants are obtained from field data (which, as previously stated, cannot for other forms of non-MIC corrosion mechanisms). However, due to limited data for MIC pitting in oil and gas equipment, the SRP pitting constants for different operational parameters can not be generated. Hence, on applying the model, the suggestion would be that the MIC pitting rate along any length of pipeline situated in any location would be the same, which is obviously inaccurate as exogenous factors play a role. Another limitation of the model is that it loses accuracy

over short durations, as shown in the case study. This is not of serious practical concern and is the nature of exponential functions.

The main idea of this work was to present a framework for how to predict the progression of internal pit depths in oil and gas pipelines and equipment. The limitations revealed in this study show the challenges of model verification/validation in corrosion studies. There are three main reasons for this. The first is due to a paucity of lab or field data. Pitting data collection requires periodic shutdowns of oil pipelines to estimate relevant parameters inside the pipeline. For a variety of reasons, this is not always possible. Second, to obtain accurate MIC pitting data, other forms of pitting would need to be controlled, a difficult task which is only possible in a laboratory setting. Third, even where there is available field data, they are typically not detailed enough to provide the depth of information needed to construct a useful overview necessary to model the pitting rate. For example, most of the published field studies do not include electrochemical parameters such as current density and potential.

A necessary next step to this work will be the construction of a comprehensive matrix of SRP pitting variables showing their interdependence and how they affect the SRP pitting constants. Previous studies have shown the interdependence of some pitting variables (Mughabghab and Sullivan, 1989; Papavinasam, Doiron and Revie, 2010; Webster, 2010; and Revie, 2015). However, a more complete study of how the various pitting variables affect one another and the SRP pitting constant is needed.

3.10 Conclusions

The proposed model provides the first link in the corrosion literature between the electrochemical principles of corrosion and their statistical applications. While there has been progress in the literature in understanding SRP corrosion, there has not been any demonstration before of how these two important aspects of SRP pitting are mathematically related. This work provides a good understanding of how the electrochemical aspects of corrosion directly interrelates with the statistical derivations of the corrosion rate, which help to predict corrosion pit growths in pipelines. In addition, this study casts doubt on the widely accepted belief that SRP pit depth and exposure time are positively linearly-related or that the SRP pitting rate and current density/corrosion potential are linearly related. By considering the effect of FeS on the biofilm of a corroding material, this model makes the case that SRP pit depth in fact increases exponentially over time. Further validation of the proposed model is required even as the shortage of long-span field corrosion data continues to pose a problem in the advancement of corrosion science.

Data Availability

The raw data required to reproduce these findings are available from first author Nonso (nonso.ezenwa@mun.ca). The processed data required to reproduce these findings are available from first author Nonso (nonso.ezenwa@mun.ca).

Acknowledgements

Authors thankfully acknowledge the financial support provided by Genome Canada and supporting partners such as Suncor, Husky, Research and Development Corporation of Newfoundland (known as Innovate NL) through large-scale applied research project grant. Author Khan acknowledge the support provided by Canada Research Chair (Tier I) program.

Overview

This chapter has been sent to a research journal for potential publication. In order to meet the criteria for Master's thesis as required by the School of Graduate Studies at Memorial University, the formatting of this chapter has been revised to the format required for Masters thesis. The content, however, remains unchanged.

CHAPTER 4

Molecular simulation study using HS^- as a parameter to assess the effect of surface deposits on the SRB-initiated pitting on metal surfaces

Nonso Ezenwa[a], Faisal Khan[a,*], Kelly Hawboldt[a], Richard Eckert[b], Torben Lund Skovhus[c]

[a)] Centre for Risk, Integrity and Safety Engineering (C-RISE)
Faculty of Engineering and Applied Science
Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada
[b)] DNV GL, 5777 Frantz Road, Dublin, OH, USA
[c)] VIA University College, Centre for Applied Research and Development in Building, Energy & Environment, Chr. M. Østergaards Vej 4, DK-8700 Horsens, Denmark

*Correspondance author: Email: fikhan@mun.ca; Tel: + 1 709 864 8939

4.1 Abstract

Studies in microbiologically influenced corrosion (MIC) have reported on the effects of pre-corrosion surface deposits on the localized pitting which occurs on metals. But due to the complexity and heterogeneity of these deposits, which include biofilms, it is necessary to investigate how the components of these deposits and the conditions therein influence the formation of pits on the metal surfaces. To gain a better understanding of the occurrence and growth of pits under these deposits, it is imperative to consider their interactions with the metal surface at the atomistic level. In this work, molecular modelling is used to study these interactions, with the focus being on parameterizing the role of HS^- in microbiologically influenced pitting. The bond length of HS^- is used as a predictive parameter in the molecular model to study the MIC interface. It is observed that changes in the HS^- bond length denote HS^- reactivity and the subsequent production of sulfides which are the main by-products of MIC. This study also shows how changes in temperature impact HS^- reactivity and thus MIC activity.

Keywords: Molecular model, microbiologically influenced corrosion, pitting, biofilm, surface interaction model

4.2 Introduction

Since microbiologically influenced corrosion (MIC) was identified as one of the main threats to asset integrity management in the oil and gas industry, numerous studies have been done to understand the reactions that occur at the corrosion interface

(Dickinson and Lewandowski, 1998; Xu, Chan and Fang, 2002; Sheng, Ting and Pehkonen, 2007; Zhang et al, 2015). While these studies have contributed to the knowledge base with respect to MIC, there are still knowledge gaps and contradictions between studies (Zarasvand and Rai, 2014; Kip and van Veen, 2015). This is largely due to the complexity of the deposits which form on the metal surface. These surface deposits include inorganic compounds from the environment and biofilms which accumulate on metals before pitting occurs (Geiser, Avci and Lewandowski, 2002; Paisse et al, 2013). In addition to its microbial communities, surface deposits on metals are composed of a heterogenous mixture of large organic molecules such as polysaccharides, proteins, lipids and nucleic acids, smaller inorganic species produced as intermediates and end-products of corrosion, metal deposits, and other metabolic products (Geiser, Avci and Lewandowski, 2002; Eckert, 2015). This results in chemical reactions which can impact the thermodynamics and kinetics of MIC development, thus making the process more difficult to understand.

More recently, a different approach to understanding corrosion-related issues from a molecular level has been proposed (Taylor and Marcus, 2015; Chew, Kuwahara and Ohno, 2018). This approach, broadly termed molecular modelling (MM), refers to theoretical or computational techniques which “provide insight into the behaviour of molecular systems” (Leach, 2001). MM can be used as a tool in corrosion studies to better understand the molecular interactions between those species which cause, accelerate or inhibit corrosion, and the substrate. This is what was done in this study. However, with the importance of corrosion management and prevention, most of the research in the

application of molecular modelling in corrosion has focused on corrosion inhibition. These studies have been successful in examining the efficacy of various corrosion inhibitors, ranking inhibitors and validating these results using experimental data (Sastri and Perumareddi, 1997; Yan et al, 2008; Liu et al, 2010; Ozcan et al, 2014; Ju et al, 2015; Mendonca et al, 2017). In comparison, fewer studies have focused on understanding the mechanism of corrosion at the molecular level. This is perhaps due to the complexity and heterogeneity of the surface deposits. In fact, an exhaustive search through the literature reveals that only two studies have attempted a molecular modelling approach towards understanding corrosion (Nunomura and Sunada, 2013; Chew, Kuwahara and Ohno, 2018). The Nunomura and Sunada study (2013) modelled the corrosion interface using O_2 and H_2O as the adsorbates. They found that both adsorbates interfere with their respective adsorptions to the Fe(100) surface. Chew, Kuwahara and Ohno (2018) used molecular modelling to study the originating site of corrosion on Fe(100) surface. Studies in other fields have used molecular modeling methods to explain gas molecule attacks on different metals including Fe (Jiang and Carter, 2004; Jiang and Carter, 2005; Spencer, Todorova and Yarovsky, 2008; Zhang et al, 2012; Luo et al, 2014; Yu et al, 2015).

The molecular simulation of the interactions occurring at the MIC interface is different from the single-species adsorption simulation studies which have been widely researched due to the complexity of the MIC environment (the interactions of multiple adsorbates and a substrate in a medium). First, a molecular model of the MIC interface is developed. The molecular model presented in this paper captures the interactions of

important adsorbates relative to a fixed substrate. The bond length of one of the adsorbates - HS^- - is identified as a suitable parameter to assess these interactions. The correlation between bond length (or bond enthalpy) and reactivity of species has been well investigated in the literature and is discussed in subsequent sections (Allen and Kirby, 1984; Jones and Kirby, 1986). Second, a simulation of interactions occurring at the MIC interface is carried out. The purpose of simulating these interactions is to study how the components and conditions of the surface deposits influence the changes that occur in the adsorbates and to understand how they may relate to the MIC process overall. Pitting on the surface of a metal is assumed to be indicated by the production of sulfides (Angell and Urbanic, 2000; Kuang et al, 2007; Paisse et al, 2013). Hence, some of the questions that a molecular simulation of the MIC interface could address include: how do the components/conditions in the deposits on metals affect the production of sulfides, if at all? And by how much? This study is limited to environments where MIC is the predominant cause of pitting, such as the inside of oil pipelines and oil wells in certain locations.

4.3 Materials and methods

The molecular modelling of MIC occurring in oil and gas pipelines involves creating a model of the interactions occurring at the corrosion interface between a steel pipeline substrate and MIC-causing adsorbates from the biofilm. Two of the constituents of the corrosion interface – the substrate and adsorbates – are examined in more detail.

4.3.1 Substrate

The substrate in a corrosion process refers to the material that is degraded (Wang and Xiong, 2014). The material of interest is carbon steel, which is composed primarily of iron. The corrosion of carbon steel can essentially be considered to be the degradation of its iron component.

Figure 4.1: MIC pits in a steel tank substrate (Stephan, n.d.)

To gain a better understanding of the surface properties of substrates, the structure of these surfaces and their atomic arrangements must be defined (Wandelt, 2012). Different planes of iron are exposed depending on how iron is cleaved. The lowest energy surfaces of iron are of the most interest as they are also the most stable surfaces. Some of the low energy surfaces of Fe identified in the literature are 100, 110, 001 and 111 (Jiang and Carter, 2005; Wang et al, 2011; Waldelt, 2012). The interactions of different

molecules with these Fe planes have been studied in the literature (Jiang and Carter, 2004; Jiang and Carter, 2005; Spencer, Todorova and Yarovsky, 2008).

The movement of adatoms along the surface of a material is referred to as diffusion. To move on different sites of the surface, adatoms need to overcome certain energy barriers. Sites with the lowest energy barriers represent the optimum path for the movement of adatoms (Maca, Kotrla and Trushin, 1999). A comparison of the optimum paths on some of these Fe surfaces are shown in Table 1.

Table 4.1: Diffusion barriers on low energy paths of some common Fe surfaces (Wang et al, 2011)

Surfaces	Diffusion barrier in low energy path (eV)
Fe(110)	0.24
Fe(001)	0.49
Fe(111)	0.97

Fe(110) has the lowest diffusion barrier of the Fe indices compared in Table 1. It is suggested that this is because of it's high surface atom density (Wang et al, 2011). This characteristic indicates a stable surface which makes it suitable for this molecular simulation work.

4.3.2 Adsorbates

Adsorbates are molecules that bind to surfaces. Some of the adsorbates that are known to play a role in MIC include O_2, H_2O, H_2S, HS^- and S^{2-} (Kuhr and van der Vlugt, 1934; Xu, 2013). However, because surface deposits exist in an aqueous environment, H_2O is considered to be a medium or solvent rather than an adsorbate (Sutherland, 2001). The molecular modelling of the interactions on the MIC interface aims to investigate how these species interact with the Fe substrate in a medium (water).

To simplify the model without losing value with respect to results, the following assumptions were made:

1. There is a correlation between the production of sulfides and corrosion rate/initiation on the MIC interface (Angell and Urbanic, 2000; Kuang et al, 2007; Paisse et al, 2013). Hence, the production of sulfides is assumed to indicate pit growth.
2. The pH at the MIC interface is neutral.
3. There is sufficient lactate in the newly formed biofilm to act as the electron donor according to the following reaction:

$$SO_4^{2-} + 2CH_3CHOHCOO^- \rightarrow 2CH_3COO^- + 2CO_2 + HS^- + OH^- + H_2O \quad (1)$$

This ensures that HS^- is produced and present both in the bulk solution and in the biofilm at the initial stage (Fu, 2013).

4. At neutral pH, HS^- is the dominant sulfide species in the bulk solution surrounding the MIC interface (Xu, 2013). Under basic conditions, S^{2-} is formed as shown below:

$$HS^- \leftrightarrow S^{2-} + H^+ \qquad (2)$$

However, under acidic conditions, H_2S is formed as shown:

$$HS^- + H^+ \leftrightarrow H_2S \qquad (3)$$

Since HS^- is present both in the bulk solution and in the biofilm before the onset of corrosion and is also an intermediate in the synthesis of other sulfides, it is a good indicator of SRB activity and hence should be present in a simplified molecular model of the MIC interface.

5. While the presence of dissolved oxygen in the biofilm does alter the metabolic pathway of SRB (sulphate-reducing bacteria) activities, SRB are known to exhibit a high degree of aerotolerance (Ramel et al, 2015). Regardless of the oxygen conditions, sulfate reduction is still known to occur. Hence, oxygen is assumed to be present and necessary at the MIC interface.

Hence, the adsorbates necessary to model a simplified MIC interface were determined to be HS^- and O_2 in a water medium. The molecular modelling of the MIC interface centers on two important concepts: the importance of HS^- in the MIC process and the correlation between bond length and the (potential) reactivity of species. These two concepts are examined further.

4.3.3 The importance of HS^- in MIC modelling

One of the sulfides produced during MIC is HS^-. It is commonly referred to as bisulfide, sulfanide or hydrosulfide (National Center for Biotechnology Information, 2018). There are several reasons why bisulfide is potentially essential in the modelling of MIC. It is the first sulfide product formed in the bulk solution and in the biofilm. During the growth phase of the microbial consortia which eventually become part of the biofilm, lactate is consumed as an energy source, as shown in equation 1. This reaction, which precedes the anodic oxidation of Fe, results in the production of HS^-. Hence, it is known to be the dominant sulfide species in the bulk solution in MIC environments (Fu, 2013; Xu, 2013). Second, HS^- is an intermediate in the formation of H_2S and S^{2-} on the surface of the substrate. Thus, changes in conditions such as pH can result in the generation of different metabolic products (Xu, 2013). Third, the cathodic (or sulfate utilization) stage in the biocatalytic sulfate reduction (BCSR) theory is believed to occur at a negligible rate, due to the innate slowness of biocatalytic reactions (Xu, 2013). This means that HS^- is a product in the rate-limiting step of MIC in SRB environments, which is typically an important consideration in concentration modelling.

While molecular simulations do not consider the concentrations of adsorbates, it is obvious that HS^- plays a role in the MIC process and can be used as an indicator for the process, where no other source of sulfide is present in the environment. Consequently, this important role of HS^- is preserved in creating a simplified molecular model of the MIC interface.

4.3.4 Bond length and reactivity

The correlation between the bond length of a species and its reactivity has been the focus of several experiments over the last few decades (Allen and Kirby, 1984; Jones and Kirby, 1986). The experiments demonstrated that for a wide range of organic and inorganic molecules, the bond lengths of molecules that are broken in chemical reactions are indicative of the reactivities of those molecules. This theory can be applied to the molecular modelling of the MIC interface, with the species of interest being HS^-, leading to two theoretical propositions. First, since bisulfide is essential in the MIC pathway as an intermediate, the interactions on the MIC interface must produce variations in the bond length of HS^-. Second, these variations in the bond length should correspond to the initiation or inhibition of sulfide production in the biofilm. These propositions are based on Kirby's theory on bond length-reactivity correlation in simple and complex molecules and are tested using molecular simulations at the corrosion interface.

4.3.5 Methodology

The modelling of the MIC interface is done in two phases as described below:

Phase 1: This involves the identification of the preferred adsorption sites for the adsorbates on Fe(110). Computational power is minimized when adsorbates are docked on their preferred adsorption sites for the start of simulation. Due to the number of simulations involved in this study, this was an important precursor to the dynamic simulations that followed. The adsorption locator tool in the Dmol module in Material

Studio 7.6X (installed on a desktop computer at the C-RISE Office ER-4015) was used to identify the preferred adsorption sites. The forcefield was set to COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) and the quality was set to fine for increased precision. The fixed energy window was set to the default value of 100kcal/mol.

Phase 2: This phase entails the docking of the adsorbates to their preferred adsorption sites, based on the results obtained from phase 1. This is followed by the geometric optimization of the system in order to determine its most stable structure. Geometric optimization is carried out at a functional of GGA PW91 and was spin restricted. In a trade-off between speed and accuracy, the integration accuracy and SCF tolerance were set to coarse. Because MIC takes place in solution, a solvation model was used for the simulation, with smearing set to the maximum 10.0 Ha to allow for full convergence. The solvent used was water. The Fe(110) surface was fixed since the phenomenon of interest are the interactions of the adsorbates relative to the substrate. The result of the optimization is the structure shown in Figure 4.2. The bond lengths of the adsorbates are shown. Since the adsorbates are linear molecules, bond angles are not applicable.

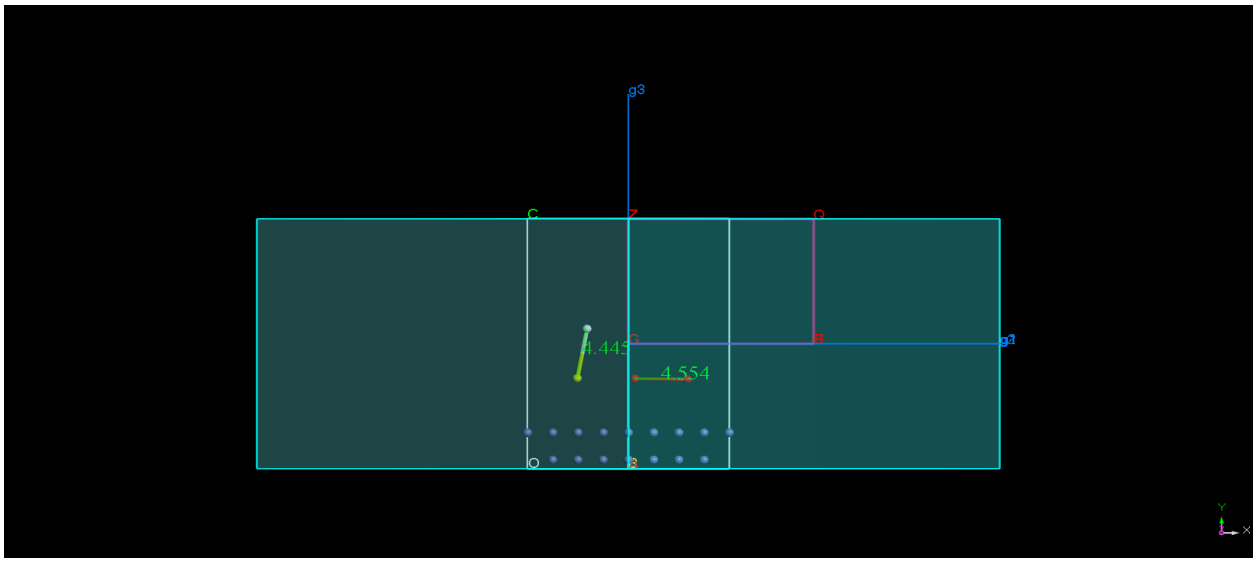

Figure 4.2: The molecular model of the MIC interface

4.4 Results and Discussion

Figure 4.2 shows the optimized structure of the MIC interface. This comprises the Fe(110) substrate surface (the purple balls), oxygen molecule (the red balls), bisulfide (the white ball of hydrogen bonded to the yellow ball representing a sulfur atom) and the water medium (the light blue haze). This is the most stable (lowest energy) form of this structure obtained after geometric optimization, as described previously. The model, though a simplified representation of an MIC interface which really comprises a wide array of organic and inorganic molecules, offers some insight into the interactions that occur here based on the orientations of the molecules. The electronegative end of the HS^- molecule is oriented towards the cleaved Fe(110) surface, while the oxygen atoms lie roughly on the same horizontal plane, as is to be expected.

The adsorption energies of HS^- and O_2 on Fe(110), determined by using the absorption locator module in Material Studio, are shown in Table 4.2.

Table 4.2: Energies of adsorption on Fe(110) by MIC adsorbates obtained from phase 1

	Deformation energy (kcal/mol)	Rigid adsorption energy (kcal/mol)	Adsorption energy (kcal/mol)	Total Energy (kcal/mol)
H-S^- on Fe(110)	-1.39	-9.93	-11.33	-9.93
O=O on Fe(110)	-4.35	-13.75	-18.11	-13.75

Techniques typically used for the direct measurement of the adsorption energies of adsorbates on substrates include ellipsometry, differential scanning calorimetry (DSC) and quartz crystal microbalance (QCM) (Sancaktar et al, 2016). Quantum mechanical techniques are reported to be inaccurate but are considered sufficient for comparison purposes, as is the case here (Krishtalik, 2016). The adsorption locator provides information about preferred adsorption sites as well as adsorption energies of HS^- and O_2 on Fe(110). The adsorption energies of both adsorbates to Fe(110) are negative showing that there is attraction between them, with the greater attraction observed between O_2 and Fe(110). Both energies fall below what would be expected for chemisorption but lie within physisorption levels. This explains why subsequent dynamics simulations do not show any bond breakages, as would be the case in chemisorption.

4.4.1 Validation using dynamics simulation

The conditions on the substrate influence the occurrence of microbially initiated pits. Some of these conditions include the presence and concentrations of microbial communities and molecules, as well as external factors such as temperature. Temperatures within oil pipelines are usually maintained within a certain range. Crude oil being transported through the Trans-Pacific pipeline network is typically heated electromagnetically to reduce oil viscosity and increase fluid flow. The increased flow results in higher throughput volumes for the crude and reduced costs. It is reported that pipelines in the Pacific System are usually kept at temperatures between 291.8K and 355.2K (Shauers et al, 2000; Dunia and Edgar, 2012). However, heating transported crude is believed to increase the incidence of corrosion and the pitting rates in oil pipelines as shown in Figure 4.3 (Perez, 2013).

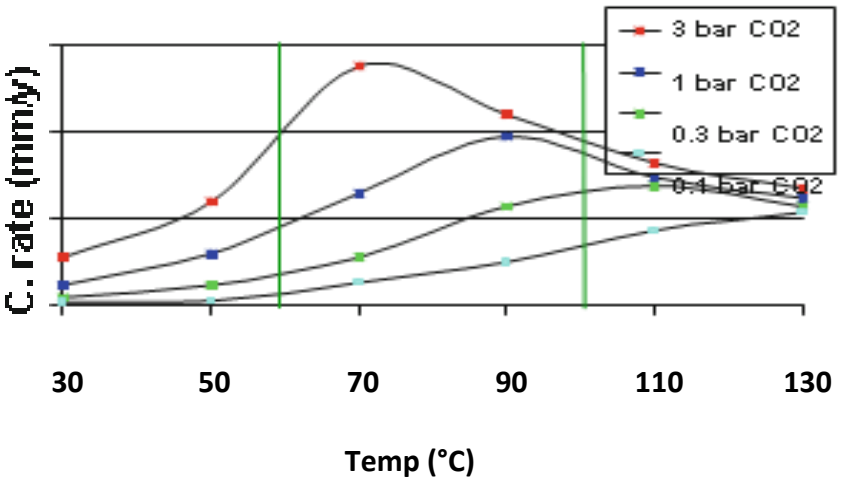

Figure 4.3: Effect of temperature on the corrosion rate (Perez, 2013)

The min-max temperatures cited above were used as boundary temperatures in molecular dynamics simulations. The NVT ensemble dynamics simulations of the molecular model of the MIC interface was carried out at various temperatures between 291.8K and 355.2K. The selected temperatures were 310K, 330K and 345K, in addition to the boundary temperatures. Once again, the simulations were carried out at a functional of GGA PW91 and was spin restricted. The integration accuracy and SCF tolerance were set to coarse. A solvation model was used with smearing set to 10.0 Ha. The solvent used was water. The simulation results are summarized in Table 4.3.

Table 4.3: The effect of temperature changes on the bond lengths of the adsorbates on the MIC interface

Temperature (K)	O=O bond length (in Angstroms)	$H\text{-}S^-$ bond length (in Angstroms)
Optimized	4.554	4.445
291.8	5.413	3.260
310	5.421	4.863
330	4.613	11.436
345	5.503	16.874
355.2	4.480	18.089

The results in Table 4.3 show that the HS^- bond length increases with increasing temperature. Based on Kirby's experiments and bond-reactivity theory, there is a positive correlation between the HS^- bond length and the reactivity of HS^- to produce sulfides. (It is noteworthy to remember that pitting on the MIC interface is marked by the formation of sulfides, typically FeS and H_2S, which change the electrochemistry of the biofilm). Hence, as the bond length increases with increasing temperature, there is an increase in

the chemical reactivity of this intermediate leading to a rise in sulfide production on the MIC interface. Simply put, as the HS^- bond length increases, the potential for pit growth on the surface of metals increases as well. This shows that the changes in the bond length of HS^-, which is an important MIC intermediate, can be an indicator of sulfide production in the surface deposits in corrosion systems where SRB is active. This can potentially be used to evaluate the acceleration/inhibition properties of molecules and conditions in the biofilm, which is currently an area where there is a lack of clarity.

4.5 Conclusion and further research direction

This preliminary study proposes a simplified molecular model of the MIC interface. This model uses changes in the bond length of an adsorbate in the model - HS^- - to predict sulfide production on the MIC interface. Pipeline temperature was used as a variable to show how this model can be applied. The deposits on the surface of metals contain a wide array of organic and inorganic substances which are used to sustain microbial life, as well as substances that are produced because of microbial activities. Some of these include metal ions, inorganic compounds, polysaccharides and organic acids. There are other molecules in the deposit which have been suggested in the literature to both accelerate and inhibit microbially initiated pitting, such as lactate and phosphate salts (Javed et al, 2014; Xu, 2013). This lack of clarity does not help in the understanding of the process. Molecular simulation of the MIC interface offers a possible alternative to experimentation. Some of the conclusions of this study include the following:

- To better understand the problem of localized pitting in pipelines in SRB environments, it may be necessary to adopt a more specific and less holistic approach. The holistic approach considers how deposits in various environments influence pitting while a more specific method investigates the effect on surface pitting of the components and conditions in a typical deposit.
- This more specific approach can be achieved by the molecular simulation of the MIC interface. A first step in simulating the interactions on the interface is the development of a simplified molecular model of the MIC interface followed by the molecular simulation of interface interactions.
- To make sense of the molecular interactions, an indicator is needed. The bond length of HS^- was identified as a suitable indicator of the production of sulfides on the MIC interface, which is assumed to be a good measure of surface pitting.

To extend this model to test for the effect of molecules such as lactate or phosphates on microbially initiated pitting, certain changes to the optimized structure of the MIC interface may need to be made. What this preliminary study shows is how this can be achieved. Future areas of research should include simulating the effects of some of these molecules, and possibly other external conditions in the biofilm such as pH, on surface pitting on metals. Knowledge gained from this could find useful applications in corrosion inhibition studies. The identification of what components of surface deposits contribute to pitting and by how much, would lead to more targeted and effective MIC management, prevention and control.

Acknowledgements

Authors thankfully acknowledge the financial support provided by Genome Canada and supporting partners such as Suncor, Husky, Research and Development Corporation of Newfoundland (known as Innovate NL) through large-scale applied research project grant. Author Khan acknowledges the support provided by the Canada Research Chair (Tier I) program.

Chapter 5

Conclusions

In conclusion, the modelling of microbiologically influenced corrosion can yield many useful insights and improve the understanding of asset integrity of oil field infrastructure and equipment. These insights are discussed under study observations and future recommendations.

5.1 Review of important observations

The modelling of MIC in this thesis work was done using two different approaches: a mechanistic modelling approach and a molecular modelling approach. The main contributions of both approaches are outlined below:

- By mathematical modelling, this work establishes that pit depth varies exponentially with time. While this had been suggested in the literature, this work provides a mathematical basis for this assumption.
- This thesis work introduces the concept of MIC pitting constants in corrosion studies.
- It proposes a predictive model which calculates the average pit depth at any point on the surface of a material, based on the age of the material and the MIC constant of its effluent environment.

- It demonstrates how the proposed MIC constants can be generated and used to predict the MIC pit depth over time.
- It shows how these MIC constants would vary across different environments which would result in differing pitting rates.
- The proposed MIC model is one of the few time-dependent models in the corrosion literature.
- This work also proposes a molecular model of the MIC interface as the basis of atomistic simulations of surface interactions leading to corrosion
- Using the molecular model of the MIC interface, it demonstrates a method for evaluating the effect of biofilm conditions on the pitting rate.
- The molecular simulation of the interactions occurring at the surface of the material can shed some light on issues of contention about the role of biofilms in MIC.

5.2 Future research directions

The two-prong modelling approach to MIC creates new knowledge opportunities in corrosion studies. Some of these research opportunities are discussed below:

- The proposed models in this thesis need further validation through controlled lab experiments and molecular simulations. It may then be possible to extend the applications of these models to field settings under the right conditions.

- Despite exhaustive efforts to identify relevant MIC pitting data in the literature, none was found. To generate a matrix of reliable MIC pitting constants necessary to accurately predict pit depths over time, controlled lab data for MIC pitting is required. This is an important area for further research.
- The atomistic simulation of the MIC interface involving more adsorbates than the two used in this simulation work is also necessary.

Bibliography

Al-Darbi, M.M., Agha, K., and Islam, M.R. (2005). Comprehensive modelling of the pitting biocorrosion of steel. *The Canadian Journal of Chemical Engineering, 83*: 872-881

Al-Jaroudi, S.S., Ul-Hamid, A., and Al-Gahtani, M.M. Failure of crude oil pipeline due to microbiologically induced corrosion. (2011). *Corrosion Engineering, Science and Technology, 46(4)*: 568-579

Allen, F.H., and Kirby, A.J (1984). Bond length and reactivity: Variable length of the C-O single bond. *Journal of American Chemical Society, 106:* 6197-6200

Andrade, C., and Gonzalez, J.A. (1978). Quantitative measurements of corrosion rate of reinforcing steels embedded in concrete using polarization resistance measurements. *Werkstoffe und Korrosion, 29*: 515-519

Beech, I.B., and Sunner, J. (2004). Biocorrosion: Towards understanding interactions between biofilms and metals. *Current Opinion in Biotechnology, 15:* 181-186

Bhandari, J., Khan, F., Abbassi, R., Garaniya, V., and Ojeda, R. (2015). Modelling of pitting corrosion in marine and offshore steel structures – A technical review. *Journal of Loss Prevention in the Process Industries, 37:* 39-62

Bhat, S., Kumar, B., Prasad, S.R., and Katarki, M.V. (2011). Failure of a new 8-in pipeline from Group Gathering Station to Central Tank Farm. *Materials Performance, 50(5):* 50-54

Biezma, M.V. (2001). The role of hydrogen in microbiologically influenced corrosion and stress corrosion cracking. *International Journal of Hydrogen Energy, 26:* 515-520

Booth, G.H., Elford, L., and Wakerley, D.S. (1968). Corrosion of mild steel by sulphate-reducing bacteria: An alternative mechanism. *British Corrosion Journal, 3(5):* 242-245

Booth, G.H., and Tiller, A.K. (1968). Cathode characteristics of mild steel in suspensions of sulphate-reducing bacteria. *Corrosion Science, 8:* 583-600

Borenstein, S.W. (1994). *Microbially Influenced Corrosion Handbook.* Cambridge, England: Woodhead Publishing.

Caines, S., Khan, F., and Shirokoff, J. (2013). Analysis of pitting corrosion on steel under insulation in marine environments. *Journal of Loss Prevention in the Process Industries, 26:* 1466-1483

Caleyo, F., Velazquez, J.C., Valor, A., and Hallen, J.M. (2009). Markov chain modelling of pitting corrosion in underground pipelines. *Corrosion Science, 51:* 2197-2207

Chew, K., Kuwahara, R., and Ohno, K. (2018). First-principles study on the atomistic corrosion processes of iron. *Physical Chemistry Chemical Physics, 20:* 1653-1663

Coetser, S.E., and Cloete, T.E. (2005). Biofouling and biocorrosion in industrial water systems. *Critical Reviews in Microbiology, 31:* 213-232

Davis, J.R. (2000). *Corrosion: Understanding the basics.* OH, US: ASM International

Davydov, A.D. (2007). Analysis of pitting corrosion rate. *Russian Journal of Electrochemistry, 44(7):* 835-839

Dickinson, W.H., and Lewandowski, Z. (1998). Electrochemical concepts and techniques in the study of stainless steel ennoblement. *Biodegradation, 9:* 11-21

Dunia, R., and Edgar, T.F. (2012). Study of heavy crude oil flows in pipelines with electromagnetic heaters. *Energy Fuels, 26:* 4426-4437

Eckert, R.B. (2015). Emphasis on biofilms can improve mitigation of microbiologically influenced corrosion in oil and gas industry. *Corrosion Engineering, Science and Technology, 50(3):* 163-168

Edyvean, R.G.J., Benson, J., Thomas, C.J., Beech, I.B., and Videla, H.A. (1998). Biological influences on hydrogen effects in steel in seawater. *Materials Performance, 37(4):* 40-44

Enning, D., and Garrelfs, J. (2014). Corrosion of iron by sulfate-reducing bacteria: New views of an old problem. *Applied and Environmental Microbiology, 80(4):* 1226-1236

Eroini, V., Oehler, M.C., Graver, B.K., Mitchell, A., Lonvik, K., Skovhus, T.L. (2017). *Investigation of amorphous deposits and potential corrosion mechanisms in offshore water injection systems.* Paper presented at the NACE International Corrosion Conference and Expo 2017, paper no. 9433

Fang, H.H.P., Xu, L.C., and Chan, K.Y. (2002) Effect of toxic metals and chemicals on biofilm and biocorrosion. *Water Research, 36*: 4709-4716

Fu, C., Zheng, J., Zhao, J., and Xu, W. (2001). Application of grey relational analysis for corrosion failure of oil tubes. *Corrosion Science, 43:* 881-889

Fu, W. (2013). Investigation of Type II of Microbiologically Influenced Corrosion (MIC) mechanism and mitigation of MIC using novel green biocide cocktails (Masters thesis). Russ College of Engineering and Technology, Ohio University, Ohio, USA

Gall, J.L., and Xavier, A.V. (1996). Anaerobes response to oxygen: The sulphate-reducing bacteria. *Anaerobe, 2:* 1-9

Gan, F., Tian, G., Wan, Z., Liao, J., and Li, W. (2016). Investigation of pitting corrosion monitoring using field signature method. *Measurement, 82*: 46-54

Gayosso, M.J.H., Olivares, G.Z., Ordaz, N.R., Ramirez, C.J., Esquivel, R.G., and Viveros, A.P. (2004). Microbial consortium influence upon steel corrosion rate, using polarization resistance and electrochemical noise techniques. *Electrochemica Acta, 49:* 4295-4301

Geiser, M., Avci, R., and Lewandowski, Z. (2002). Microbially initiated pitting on 316L stainless steel. *International biodeterioration and biodegradation, 49:* 235-243

Gong, Y., Tang, J., and Zhao, D. (2016). Application of iron sulfide particles for groundwater and soil remediation: A review. *Water Research, 89*: 309-320

Gramp, J.P., Bigham, J.M., Jones, F.S., Tuovinen, O.H. (2010). Formation of Fe-sulfides in cultures of sulfate-reducing bacteria. *Journal of Hazardous Materials, 175:* 1062-1067

Groysman, A. (2010). *Corrosion for Everybody.* Dordrecht, Germany: Springer

Gu, T., Zhao, K., and Nesic, S. (2009). *A new mechanistic model for MIC based on a biocatalytic cathodic sulfate reduction theory*. Paper presented at NACE corrosion conference and expo. Paper no. *09390.*

Hamilton, W.A. (2003). Microbially influenced corrosion as a model system for the study of metal microbe interactions: A unifying electron transfer hypothesis. *Biofouling, 19(1):* 65-76

Hehre, W.J. and Shusterman, A.J. (2000). *Molecular modelling in undergraduate Chemistry education.* USA: Wavefunction Inc.

Heidersbach, R. (2011). *Metallurgy and Corrosion Control in Oil and Gas Production.* New Jersey, USA: John Wiley & Sons

Huang, F., Li, X.G., Liu, J., Qu, Y.M., Jia, J., and Du, C.W. (2011). Hydrogen-induced cracking susceptibility and hydrogen trapping efficiency of different microstructure X80 pipeline steel. *Journal of Materials Science, 46(3):* 715-722

Ivarson, K.C., and Hallberg, R.O. (1976). Formation of mackinawite by the microbial reduction of jarosite and its application to tidal sediments. *Geoderma, 16:* 1-7

Jack, T.R., Wilmott, M., Stockdale, J., van Boven, G., Worthingham, R.G., Sutherby, R.L. (1998). Corrosion consequences of secondary oxidation of microbial corrosion. *Corrosion, 54(3):* 246-252

Jacobson, G.A. (2007). Corrosion at Prudhoe Bay – A lesson on the line. *Materials Performance, 46(8):* 26-34

Javed, M.A., Stoddart, P.R., Palombo, E.A., McArthur, S.L., and Wade, S.A. (2014). Inhibition or acceleration: Bacterial test media can determine the course of microbiologically influenced corrosion. *Corrosion Science, 86:* 149-158

Jiang, D.E., and Carter, E.A. (2004). Adsorption, diffusion and dissociation of H_2S on Fe(100) from first principles. *Journal of Physical Chemistry B, 108:* 19140-19145

Jiang, D.E., and Carter, E.A. (2005). First principles study of H_2S adsorption and dissociation on Fe(110). *Surface Science, 583:* 60-68

Jones, D.A. (1996). *Principles and Prevention of Corrosion*. NJ, US: Prentice Hall.

Jones, P.G., and Kirby, A.J. (1986). Multiple bond length-reactivity correlations. *Journal of the Chemical Society, Chemical Communications:* 444-445

Ju, H., Chen, J., Sun, C., and Li, Y. (2016). Quantum chemical studies on some new bipyrazole derivatives as corrosion inhibitors for steel materials. *Anti-corrosion methods and materials, 63(3):* 231-235

Kakooei, S., Ismail, M.C., and Ariwahjoedi (2012). Mechanisms of microbiologically influenced corrosion: A review. *World Applied Sciences Journal, 17(4):* 524-531

Kato, S. (2015). Biotechnological aspects of microbial extracellular electron transfer. *Microbes and Environments, 30(2):* 133-139

Kiefner, J.F., and Kolovich, K.M. (2007). Calculation of a corrosion rate using Monte Carlo Simulation. *NACE International Corrosion Conference and Expo, 07120.*

Kip, N., and van Veen, J.A. (2015). The dual role of microbes in corrosion. *International Society for Microbial Ecology, 9:* 542-551

Krishtalik, L.I. (2016). The hydrogen overpotential – hydrogen adsorption energy relationship. A new approach to the problem. *Electrochimica Acta, 218:* 125-132

Kuhr, C.A.H.W., and van der Vlugt, L.S. (1934). Graphitization of cast-iron as an electro-biochemical process in anaerobic soils. *Water, 18(16);* 147-165

Larsen, J., Holmkvist, L., Sorensen, K., and Skovhus, T.L. (2011). Identification and quantification of microorganisms Involved in downhole MIC in a Dan oil producing well. *NACE International Corrosion Conference and Expo, 11223.*

Leach, A.R. (2001). *Molecular modelling: Principles and applications (2nd).* Essex, England: Pearson Education Limited

Liengen, T., Feron, D., Basseguy, R., and Beech, I.B. (2014). *Understanding Biocorrosion: Fundamentals and Applications.* Cambridge, UK: Woodhead Publishing Limited.

Little, B., and Ray, R. (2002). A perspective on corrosion inhibition by biofilms. *Corrosion, 58(5)*: 424-428.

Little, B.J., and Lee, J.S. (2007). *Microbiologically influenced corrosion.* Hoboken, NJ: John Wiley and Son's, Inc.

Liu, J., Yu, W., Zhang, J., Hu, S., You, L., and Qiao, G. (2010). Molecular modelling study on inhibition performance of imidazolines for mild steel in CO_2 corrosion. *Applied Surface Science, 256:* 4729-4733.

Liu, S., Liu, G., Zhong, Y., Wang, F., Ma, Z., Zhang, Y., and Huang, J. (2004). Transformation characteristics of medium carbon V-Ti-N microalloyed steel for non-quenched/tempered oil well tubes. *Materials Science and Technology, 20:* 357-362

Liu, Q., Liu, B., Li, W., Zhao, X., Zuo, W., and Xing, D. (2017). Impact of ferrous iron on microbial community of the biofilm in microbial fuel cells. *Frontiers in Microbiology, 8(920)*

Luo, H., Cai, J., Tao, X., and Tan, M. (2014). Adsorption and dissociation of H_2S on Mo(100) surface by first-principles study. *Applied Surface Science, 292:* 328-335

Maca, F., Kotrla, M., and Trushin, O.S. (1999). Energy barriers for diffusion on stepped Pt(111) surface. *Vacuum, 54:* 113-117

Machuca, L.L., Bailey, S.I., and Gubner, R. (2012). Systematic study of the corrosion properties of selected high-resistance alloys in natural seawater. *Corrosion Science, 64:* 8-16

Machuca, L.L., Bailey, S.I., Gubner, R., Watkin, E., Kaksonen, A., Heidersbach, K. (2013). Effect of oxygen and biofilms on crevice corrosion of UNS S31803 and UNS N08825 in natural seawater. *Corrosion Science, 67:* 242-255

Machuca, L.L., Jeffrey, R., Bailey, S.I., Gubner, R., Watkin, E.L.J., Ginige, M.P., Kaksonen, A.H., and Heidersbach, K. (2014). Filtration-UV irradiation as an option for mitigating the risk of microbiologically influenced corrosion of subsea construction alloys in seawater. *Corrosion Science, 79:* 89-99

Malvankar, N.S., Tuominen, M.T., and Lovley, D.R. (2012). Biofilm conductivity is a decisive variable for high-current-density *Geobacter sulferreducens* microbial fuel cells. *Energy and Environment Science, 5*: 5790-5797

Manafi, Z., Hashemi, M., Abdollahi, H., and Olson, G.J. (2013). Biocorrosion of water pipeline by sulfate-reducing bacteria in a mining environment. *African Journal of Biotechnology, 12(46):* 6504-6516.

Melchers, R.E. (2007). Transition from marine immersion to coastal atmospheric corrosion for structural steels. *Corrosion, 63(6):* 500-514

Melchers, R.E. (2010). Estimating uncertainty in maximum pit depth from limited observational data. *Corrosion Engineering, Science and Technology, 45(3):* 240-248

Mendonca, G.L.F., Costa, S.N., Freire, V.N., Casciano, P.N.S., Correira, A.N., de Lima-Neto, P. (2017). Understanding the corrosion inhibition of carbon steel and copper in sulphuric acid medium by amino acids using electrochemical techniques allied to molecular modelling methods. *Corrosion Science, 115:* 41-55

Mohd, H.M., and Paik, J.K. (2013). Investigation of the corrosion progress characteristics of offshore subsea oil well tubes. *Corrosion Science, 67:* 130-141

Morse, J.W., Millero, F.J., Cornwell, J.C., and Rickard, D. (1987). The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. *Earth Science Reviews, 24:* 1-42

Mughabghab, S.F., and Sullivan, T.M. (1989). Evaluation of the pitting corrosion of carbon steels and other ferrous metals in soil systems. *Waste Management, 9:* 239-251

Muthukumar, N., Rajasekar, A., Ponmarriapan, S., Mohanan, S., Maruthamuthu, S., Muralidharan, S., Subramanian, P., Palaniswamy, N., and Raghavan, M. (2003). Microbially influenced corrosion in petroleum product pipelines – A review. *Indian Journal of Experimental Biology, 41:* 1012-1022

NACE International. (2016). *International Measures of Prevention, Application and Economics of Corrosion Technologies Study.* NACE International Impact, Houston, TX, 2016

National Center for Biotechnology Information, PubChem Compound Database; CID=5047209 https://pubchem.ncbi.nlm.nih.gov/compound/5047209 (accessed Aug. 7, 2018).

Newman, R.C., Rumash, K., and Webster, B.J. (1992). The effect of pre-corrosion on the corrosion rate of steel in neutral solutions containing sulphide: Relevance to microbially influenced corrosion. *Corrosion Science, 33(12):* 1877-1884

Nessim, M., Dawson, J., Mora, R., and Hassanein, S. (2008). Obtaining corrosion growth rates from repeat in-line inspection runs and dealing with the measurement uncertainties. *Proceedings of the 7th International Pipeline Conference, IPC2008-64378*

Nunomura, N., and Sunada, S. (2013). Density functional theory-based modelling of the corrosion on iron surfaces. *Archives of Metallurgy and Materials, 58(2):* 321-323

Obuekwe, C.O., Westlake, D.W.S., Plambeck, J.A., and Cook, F.D. (1981). Corrosion of mild steel in cultures of ferric iron reducing bacterium isolated from crude oil II. Mechanism of anodic depolarization. *Corrosion, 37, 11:* 632-637

Oguzie, E.E., Agochukwu, I.B., and Onuchukwu, A.I. (2004). Monitoring the corrosion susceptibility of mild steel in varied soil textures by corrosion product count technique. *Materials Chemistry and Physics, 84:* 1-6

Ozcan, M., and Dehri, I. (2004). Electrochemical and quantum chemical studies of some sulphur-containing organic compounds as inhibitors for the acid corrosion of mild steel. *Progress in Organic Coatings, 51:* 181-187

Ozcan, M., Toffoli, D., Ustunel, H., and Dehri, I. (2014). Insights into surface adsorbate interactions in corrosion inhibition processes at the molecular level. *Corrosion Science, 80:* 482-486

Paisse, S., Ghiglione, J., Marty, F., Abbas, B., Gueune, H., Amaya, J.M.S., Muyzer, G., and Quillet, L. (2013). Sulfate-reducing bacteria inhabiting natural corrosion deposits from marine steel structures. *Applied Microbiological Biotechnology, 97:* 7493-7504

Palmer, A.C., and King, R.A. (2008). *Subsea Pipeline Engineering, 2nd Ed.* Tulsa, OK: PennWell Corporation.

Papavinasam, S., Doiron, A., and Revie, R.W. (2010). Model to predict internal pitting corrosion of oil and gas pipelines. *Corrosion, 66(3):* 1-11

Peng, C.G., Suen, S.Y., and Park, J.K. (1994). Modelling of anaerobic corrosion influenced by sulfate-reducing bacteria. *Water Environment Research, 66(5):* 707-715

Pedersen, A., and Hermansson, M. (1989). The effects of metal corrosion by *Serratia marcescens* and a *Pseudomonas sp. Biofouling, 1(4):* 313

Pedersen, A., and Hermansson, M. (1991). Inhibition of metal corrosion by bacteria. *Biofouling, 3(1):*

Pedersen, A., Kjelleberg, S., and Hermansson, M. (1988). A screening method for bacterial corrosion of metals. *Journal of Microbiological Methods, 1:* 191

Rammel, F., Brasseur, G., Pieulle. L., Valette, O., Hirschler-Rea, A., Fardeau, M.L., and Dolla, A. (2015). Growth of the obligate anaerobe *Desulfovibrio vulgaris* Hildenborough under continuous low oxygen concentration sparging: Impact of the membrane-bound oxygen reductases. *PLOS ONE,* Downloadable from DOI:10.1371/journal.pone.0123455

Revie, R.W. (2015). *Oil and Gas Pipelines Integrity and Safety Handbook.* Hoboken, NJ: John Wiley and Sons Inc.

Rivas, D., Caleyo, F., Valor, A., Hallen, J.M. (2008). Extreme value analysis applied to pitting corrosion experiments in low carbon steel: Comparison of block maxima and peak over threshold approaches. *Corrosion Science, 50:* 3193-3204

Roberge, P.R. (2000). *Handbook of Corrosion Engineering*. New York, NY: McGraw-Hill

Sancaktar, E., Bakan, M., Chang, I., Satam, S., and Farahati, R. (2016). Measurement of adsorption energy using a solid adsorbent and a liquid adsorbate using differential scanning calorimetry. *Polymer Testing, 56:* 185-191

Sastri, V.S., and Perumareddi, J.R. (1997). Molecular orbital theoretical studies of some organic corrosion inhibitors. *Corrosion, 63(8):* 617-622

Shauers, D., Sarkissian, H., Decker, B., Wilkerson, B., and Mecham, T. (2000). California line beats odds, begins moving viscous crude oil. *Oil and Gas Journal, 98(15);* 54-63

Shekari, E., Khan, F., and Ahmed, S. (2016). A predictive approach to fitness-for-service assessment of pitting corrosion. *International Journal of Pressure Vessels and Piping, 137:* 13-21

Sheng, X., Ting, Y.P., and Pehkonen, S.O. (2007). The influence of sulfate-reducing bacteria biofilm on the corrosion of stainless steel AISI 316. *Corrosion Science, 49:* 2159-2176

Shu-Lin, Z., Hui-Xian, W., and Cheng, D. (2014). Synthesis and electrical conductivity of nanocrystalline tetragonal FeS. *Chinese Physical Society, 23(8)*: 1-5

Skovhus, T.L., Andersen, E.S., and Hillier, E. (2018). Management of microbiologically influenced corrosion in risk-based inspection analysis. *SPE Production and Operations, SPE(179930):* 121-130

Skovhus, T.L., Eckert, R.B. and Rodrigues, E. (2017). Management and control of microbiologically influenced corrosion in the oil and gas industry – Overview and a North Sea case study. *Journal of Biotechnology, 256:* 31-45

Skovhus, T.L., and Holmkvist, L., Andersen, K., Pedersen, H., and Larsen, J. (2012, May). *MIC risk assessment of the Halfdan oil export spool*. Paper presented at the SPE international conference and exhibition on oilfield corrosion held in Aberdeen, UK.

Spencer, M.J.S., Todorova, N., and Yarovsky, I. (2008). H_2S dissociation on the Fe(100) surface: An ab initio molecular dynamics study. *Surface Science, 602:* 1547-1553

Stephan, B. (n.d.). Root causes and contributing factors of gas and liquid pipeline failures. *Metropolitan Forensics, Consulting, Engineering and Environmental Services.* Retrieved from https://sites.google.com/site/metropolitanforensics/root-causes-and-contributing-factors-of-gas-and-liquid-pipeline-failures

Stevenson, B.S., Drilling, H.S., Lawson, P.A., Duncan, K.E., Parisi, V.A., and Suflita, J.M. (2011). Microbial communities in bulk fluids and biofilms of an oil facility have similar composition but different structure. *Environmental Microbiology, 13(4):* 1078-1090

Sun, W., and Nesic, S. (2009). A mechanistic model of uniform hydrogen sulfide/carbon dioxide corrosion of mild steel. *Corrosion, 65(5):* 291-307

Sutherland, I.W. (2001). The biofilm matrix – An immobilized but dynamic microbial environment. *Trends in Microbiology, 9(5);* 222-227

Tan, J.L., Goh, P.C., and Blackwood, D.J. (2017). Influence of H_2S-producing chemical species in culture medium and energy source starvation on carbon steel corrosion caused by methanogens. *Corrosion Science, 119:* 102-111

Taylor, C.D., and Marcus, P. (2015). *Molecular modelling of corrosion processes: Scientific development and Engineering applications.* New Jersey, USA: John Wiley and Sons

Thauer, R.K., Kaster, A., Goenrich, M., Schick, M., Hiromoto, T., and Shima, S. (2010). Hydrogenases from methanogenic archaea, nickel, a novel cofactor and H_2 storage. *Annual Review of Biochemistry, 79:* 506-536

Usher, K.M., Kaksonen, A.H., Cole, I., and Marney, D. (2014). Critical Review: Microbially influenced corrosion of buried carbon steel pipes. *International Biodeterioration and Biodegradation, 93:* 84-106

Usher, K.M., Kaksonen, A.H., and Macleod, I.D. (2014). Marine rust tubercles harbour iron corroding archaea and sulphate reducing bacteria. *Corrosion Science, 83*: 189-197

Vanaei, H.R., Eslami, A., and Egbewande, A. (2017). A review on pipeline corrosion, in-line inspection (ILI) and corrosion growth rate models. *International Journal of Pressure Vessels and Piping, 149:* 43-54

Velazquez, J.C., Caleyo, F., Valor, A., and Hallen, J.M. (2009). Predictive model for pitting corrosion in buried oil and gas pipelines. *Corrosion, 65(5):* 332-342

Videla, H.A. (2001). Microbially induced corrosion: An updated review *International Biodeterioration and Biodegradation, 48:* 176-201

Videla, H.A., and Herrera, L.K. (2005). Microbiologically influenced corrosion: Looking to the future. *International Microbiology, 8:* 169-180

Videla, H.A., and Herrera, L.K. (2009). Understanding microbial inhibition of corrosion: A comprehensive review. *International Biodeterioration and Biodegradation, 63:* 896-900

Wandelt, K. (2012). *Surface and Interface Science 1: Concepts and Methods.* Weinheim, Germany: Wiley.VCH Verlag & Co.

Wang, C., Chang, D., Tang, C., Su, J., Zhang, Y., and Jia, Y. (2011). Single adatom adsorption and diffusion on Fe surfaces. *Journal of Modern Physics, 2:* 1067-1072

Wang, H., and Liang, C.H. (2007). Effect of sulfate reduced bacterium on corrosion behaviour of 10CrMoAl steel. *Journal of Iron and Steel Research International, 14(1):* 74-78

Wang, N., and Xiong, D. (2014). Superhydrophobic membranes on metal substrate and their corrosion protection in different corrosive media. *Applied Surface Science, 305:* 603-608

Watson, J.H.P., Cressey, B.A., Roberts, A.P., Ellwood, D.C., Charnock, J.M., and Soper, A.K. (2000). Structural and magnetic studies on heavy-metal-adsorbing iron sulphide nanoparticles produced by sulfate-reducing bacteria. *Journal of Magnetism and Magnetic Materials 214:* 13-30

Webster, D (2010). Pipeline construction drivers, corrosion costs and engineering issues. Retrieved from http://napca.com/webfiles/NAPCA-2010%20Convention-Webster.pdf

Xu, C., Zhang, Y., Cheng, G., and Zhu, W. (2008). Pitting corrosion behaviour of 316L stainless steel in the media of sulphate-reducing and iron-oxidizing bacteria. *Materials Characterization, 59:* 245-255

Xu, D (2013). Microbiologically influenced corrosion: Mechanisms and mitigation (PhD dissertation). Russ College of Engineering and Technology, Ohio University, Ohio, USA

Xu, D., Li, Y., and Gu, T. (2016). Mechanistic modelling of biocorrosion caused by biofilms of sulfate reducing bacteria and acid producing bacteria. *Bioelectrochemistry, 110*: 52-58

Xu, L.C., Chan, K.Y., Fang, H.H.P. (2002). Application of atomic force microscopy in the study of microbiologically influenced corrosion. *Materials Characterization, 48:* 195-203

Yan, Y., Li, W., Cai, L., and Hou, B. (2008). Electrochemical and quantum chemical study of purines as corrosion inhibitors for mild steel in 1M HCl solution. *Electrochimica Acta, 53:* 5953-5960

Yu, X., Zhang, X., Tian, X., Wang, S., Feng, G. (2015). Density functional theory calculations on oxygen adsorption on the Cu_2O surfaces. *Applied Surface Science, 324:* 53-60

Yuan, S.J., and Pehkonen, S.O. (2009). Microbiologically influenced corrosion of 304 stainless steel by aerobic *Pseudomonas* NCIMB 2021 bacteria: AFM and XPS study. *Colloids and surfaces B: Biointerfaces, 59*: 87-99

Zarasvand, K.A., and Rai, V.R. (2014). Microorganisms: Induction and inhibition of corrosion in metals. *International Biodeterioration and Biodegradation, 87:* 66-74

Zhang, L., Mao, Y., Ma, J., Li, D., Shi, H., Liu, Y., and Cai, L. (2013). Effect of the chemical oxidation demand to sulfide oxidation in microbial fuel cells treating sulfide-rich wastewater. *Environmental Technology, 34(2):* 269-274

Zhang, P., Xu, D., Li, Y., Yang, K., Gu, T. (2015). Electron mediators accelerate the microbiologically influenced corrosion of 304 stainless steel by the Desulfovibrio vulgaris biofilm. *Bioelectrochemistry, 101:* 14-21

Zhang, R., Liu, H., Li, J., Ling, L., and Wang, B. (2012). A mechanistic study of H_2S adsorption and dissociation on $Cu_2O(111)$ surfaces: Thermochemistry, reaction barrier. *Applied Surface Science, 258:* 9932-9943

Zhang, Y., and Moloney, J. (2016). Electrochemical corrosion rate measurement under iron sulfide deposit. *Corrosion, 72(5):* 704-716